Ministry of Environment and Gender Equality
Environmental Protection Agency

PFAS-inator Sustainable and cost-effective technology for PFAS-removal from landfill leachate MUDP-project

MUDP Report

December 2024

Publisher: The Danish Environmental Protection Agency

Editors:
Sabine Lindholst, Teknologisk Institut
Jonathan Guld Christensen, Teknologisk Institut
Tore Svendsen, ECT2
Henrik Rasmus Andersen, DTU Sustain
Kai Tang, DTU Sustain
Maria Nymann Christensen, Aquarden Technologies

ISBN: 978-87-7038-692-0

Miljøteknologisk Udviklings- og Demonstrationsprogram

Projektet, som er beskrevet i denne rapport, er støttet af Miljøteknologisk Udviklings- og Demonstrationsprogram (MUDP) under Miljøministeriet, der støtter udvikling, test og demonstration af miljøteknologi.

MUDP investerer i udvikling af fremtidens miljøteknologi til gavn for klima og miljø i Danmark og globalt, samtidig med at dansk vækst og beskæftigelse styrkes. Programmet understøtter dels den bredere miljødagsorden, herunder rent vand, ren luft og sikker kemi, men understøtter også regeringens målsætninger inden for klima, biodiversitet og cirkulær økonomi.

Det er MUDP's bestyrelse, som beslutter, hvilke projekter der skal modtage tilskud. Bestyrelsen betjenes af MUDP-sekretariatet i Miljøstyrelsen.

MUDP-sekretariatet i Miljøstyrelsen
Tolderlundsvej 5, 5000 Odense| Tlf. +45 72 54 40 00

Mail: ecoinnovation@mst.dk
MUDP's hjemmeside

Denne slutrapport er godkendt af MUDP, men det er alene rapportens forfatter/projektlederen, som er ansvarlige for indholdet. Rapporten må citeres med kildeangivelse.

Contents

Preface

This is the final report for the project "PFAS-inator - Sustainable and cost-effective technology concept for the removal of PFAS compounds from leachate and drainage water from soil deposits" under the Danish Environmental Agency's grant ”MUDP 2020”.

The project aims to develop simple and cost-effective pretreatment and concentration technologies and combine these with supercritical oxidation (SCWO). Through this, a unique technology concept is created that is both financially affordable and at the same time completely breaks down problematic substances such as PFAS compounds.

Aquarden Technologies ApS, Vandrensning.com ApS, H2oNordic Denmark ApS, Eden Aquatech AB, Argo I/S (Audebo Landfill), Fors A/S, Perpetuum AS, Norge, Nomi4S I/S, Hjørring Vandselskab A/S, DTU Sustain and the Danish Technological Institute participated in the project.

The project was executed between February 2020 and December 2023.

Project responsible:
Tore Christian Svendsen, Vandrensning.com, PM
Rikke Markfoged, Danish Technological Institute, Adm. PM
Zhuoyan Cai, Aquarden Technologies
Steffen Boye-Hansen, H2o Nordic
Svend Kofod Petersen, Eden Aquatech
Lena Hjalholt, Argo I/S
Mette Guldborg Hansen, Fors
John Barlindhaug, Perpetuum
Hans Bloch, Nomi4S
Jacob Andersen, Hjørring Vandselskab
Henrik Rasmus Andersen, DTU Sustain

Project participants:
Andreas Baisner, Vandrensning.com
Sabine Lindholst, Jonathan Guld Christensen, Caroline Kragelund Rickers, Danish Technological Institute
Maria C. Nymann, Aquarden Technologies
Johan Flor Mortensen, Argo
Jo Løvdal Hoel, Perpetuum
Carl Ejnar Fjordside, Nomi4S
Didde Lindholm Jürgensen, Kamilla Hansen, Hjørring Vandselskab
Kamilla Marie Speht Kaarsholm, Kai Tang, DTU Sustain

The project was followed by:
Anne Mette Bräuner Lindof, Forsvarsministeriets Ejendomsstyrelse
Maria Benavent Benavent, Nanna Rørbech, Miljøstyrelsen

Aarhus, November 2023

Glossary

AIX	Anion ion exchange
AFFF	Aqueous film forming foam
AOP	Advanced oxidation processes
BV	Bed volume
CAPEX	Capital expenditure
COD	Chemical Oxygen Demand
FF	Foam fractionation
GAC	Granular activated carbon
LOD	Limit of detection
OPEX	Operation expense
PAC	Powdered activated carbon
PFAS	Per- and polyfluoroalkyl substances
PFBS	Perfluorobutanesulfonic acid
PFPeA	Perfluoropentanoic acid
PFHxS	Perfluorohexanesulfonic acid
PFHxA	Perfluorohexanoic acid
PFHpA	Perfluoroheptanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanoic acid
PFOSA	Perfluorooctane sulfonamide
6:2 FTS	6:2-Fluorotelomer sulfonate
PFDA	Perfluorodecanoic acid
PFNA	Perfluorononanoic acid
PFDoA	Perfluorododecanoic acid
PFTrDA	Perfluorotridecanoic acid
PFTeDA	Perfluorotetradecanoic acid
SCWO	Super critical water oxidation
TWI	Tolerable weekly intake
TOC	Total Organic Carbon
TOP	Total Oxidizable Precursor

Summary

The report provides an overview of PFAS (Per- and Polyfluoroalkyl Substances) and focuses on their occurrence in the environment, removal, and destruction methods. The objective of the report is to understand the variation of PFAS in leachate from landfills and the key factors affecting their removal efficiency. The primary takeaways from the report are listed below.

- PFAS is a diverse group of human-made polyfluorinated carbon compounds, containing at least one fully fluorinated carbon atom. Their useful properties include water- and oil repellence, as well as high resistance to heat and general wear. This has led to a wide range of applications in households and industries alike. The same properties make it difficult to concentrate and destroy PFAS.
- PFAS is an increasing environmental problem, originating from a range of sources. This includes industry, landfill leachate, municipal wastewater, airports, firefighting areas, the ocean, etc.
- PFAS removal and destruction is an expensive process, hence it is crucial to remove the PFAS as close to the point source as possible, to avoid dilution, which leads to larger volumes of material to be treated and therefore increased costs.
- If the sources of PFAS are diluted, they should be concentrated into small volumes before destruction, as the destruction step is expensive.
- The PFAS-contaminated sludge fraction generated in the concentration step must be minimized as much as possible, as it also needs to undergo a costly destruction process.
- PFAS from landfill leachate is most often treated using adsorption materials with a high surface-to-volume ratio, packed in columns set up at the landfill site. Common column materials include granular activated carbon (GAC) and ion-exchange resin (resin). Both types of materials exist in a range of varieties with different properties.
- The results presented in this report suggest that GAC should be replaced with resin were possible, as the resin material has a significantly higher removal efficiency.
- The chain length of the PFAS compounds influences hydrophobicity, making the shorter chain PFAS more difficult to adsorb on column material. The studies presented here confirm that the shortest chain carboxylic PFAS breaks through the columns first. PFOSA is a longer-chain PFAS that also breaks through early, probably due to its sulphonamide side group.
- In landfill leachate, organic material is present in far larger concentrations than the PFAS itself. This organic material poses a challenge, as it competes with PFAS for adsorption spots on the adsorbent material, and its considerable variation makes it difficult to predict the lifespan of the column material. The removal of organic material is crucial for extending the column's ability to remove PFAS compounds over a longer period, as well as to prevent the buildup of organic material in the columns.
- To remove organic material, the leachate is pretreated using a combination of technologies, depending on the leachate properties. Such technologies include coagulation and flocculation with PFAS-specific flocculants, flotation, ozonation, and membrane filtration. The organic material is often dissolved and difficult to oxidize, making removal efficiencies > 50 % difficult to achieve.
- To prolong the column's lifespan beyond what is achievable with organic material removal, it is possible to partially regenerate the adsorption capacity of the columns by pumping through a regeneration solution, as successfully demonstrated in this study. However, further research is required to verify the preliminary findings presented here.
- SCWO has proven very efficient for the mineralization of PFAS compounds regardless of media type, concentration, and type of PFAS compound. Aside from the test documented in this report, Aquarden has also tested concentrates from foam fractionation

and membranes, raw untreated leachate, concentrated firefighting foam solutions, and wash solutions from GAC regeneration, etc., all with similar results and destruction efficiencies above 99.99 %. The main obstacle now for onsite implementation is the capacity and throughput.

- In addition to PFAS removal, Metalsorb was used to examine the pretreatments' ability to remove heavy metals, for a possible combined removal of both PFAS and heavy metals. This proved successful in lab-scale experiments.
- Fluorescence was tested as a parameter to determine the breakthrough of sorption columns faster than traditional PFAS analysis. The preliminary studies indicate this method could be used as a supplement to monitor the saturation of sorbents which might reduce the number of costly and time-consuming traditional PFAS analyses. Further studies should be conducted to further develop the method.
- Large-scale PFAS treatment at landfills has already been implemented at several Scandinavian landfills. The treatment is affordable and can be installed in containers or an isolated tent.

Sammenfatning

Rapporten giver et overblik over PFAS (Per- and Polyfluoroalkyl Substances) og fokuserer på deres forekomst i miljøet, fjernelses- og destruktionsmetoder. Rapportens formål er at forstå variationen af PFAS i perkolat fra lossepladser og de nøglefaktorer, der påvirker deres fjerneleseffektivitet. De primære konklusioner fra rapporten er angivet nedenfor.

- PFAS er en mangfoldig gruppe af menneskeskabte polyfluorerede kulstofforbindelser, der indeholder mindst et fuldt fluoriseret kulstofatom. Deres nyttige egenskaber omfatter vand- og olieafvisning samt høj modstand mod varme og generelt slid. Dette har ført til en bred vifte af anvendelser både i husholdninger og industrier. De samme egenskaber gør det vanskeligt at opkoncentrere og destruere PFAS.
- PFAS udgør et stigende miljøproblem, som stammer fra en række kilder. Dette inkluderer industri, losseplads-sivevand, kommunalt spildevand, lufthavne, områder hvor der udføres brandbekæmpelse, havet osv.
- Fjernelse og destruktion af PFAS er en dyr process. Derfor er det afgørende at fjerne PFAS så tæt på kilden som muligt for at undgå fortynding, hvilket fører til større mængder materiale, der skal behandles, og dermed øgede omkostninger.
- Hvis kilderne til PFAS er fortyndet, bør de koncentreres i små volumener, før de destrueres, da destruktionsprocessen er dyr.
- Den PFAS-forurenede slamfraktion, der genereres i koncentrationsprocessen, skal minimeres så meget som muligt, da den også skal gennemgå den omkostningstunge destruktionsproces.
- PFAS fra losseplads-perkolat behandles som regel ved hjælp af adsorptionsmaterialer med høj overflade-til-volumen-forhold, som er pakket i kolonner opstillet på lossepladsen. Almindelige kolonnematerialer omfatter granulær aktivt kul (GAC) og ionbytteresin (resin). Begge typer materialer findes i en række forskellige varianter med forskellige egenskaber.
- Resultaterne præsenteret i denne rapport viser, at GAC bør erstattes med resin, hvor det er muligt, da resinmaterialet har en markant højere PFAS-fjernelseseffektivitet.
- Kædelængden af PFAS-forbindelserne har indflydelse på hydrofobiciteten, hvilket gør det mere vanskeligt at adsorbere PFAS med kort kædelængde på kolonnemateriale. Studierne præsenteret her bekræfter, at de korte carboxylsyrer bryder igennem først. PFOSA er en længere kæde PFAS, som også bryder igennem tidligt, sandsynligvis på grund af dens sulfonamid-sidegruppe.
- I lossepladsens perkolat er organisk materiale til stede i langt større koncentrationer end PFAS selv. Dette organiske materiale udgør en udfordring, da det konkurrerer med PFAS om adsorptionssteder på adsorptionsmaterialet, og dets betydelige variation gør det svært at forudsige levetiden for kolonnematerialet. Fjernelsen af organisk materiale er afgørende for at forlænge kolonnens evne til at fjerne PFAS-forbindelser over en længere periode samt for at forhindre opbygningen af organisk materiale i kolonnerne.
- For at fjerne organisk materiale forbehandles perkolatet med en kombination af teknologier afhængigt af sigevandets egenskaber. Sådanne teknologier omfatter koagulation og flokkulering med PFAS-specifikke flokkulanter, flotation, ozonbehandling og membranfiltrering. Organisk materiale er ofte opløst og vanskeligt at oxidere, hvilket gør det svært at opnå fjernelseseffektiviteter på over 50 %.
- For at forlænge kolonnens levetid ud over hvad der kan opnås med fjernelse af organisk materiale, er det muligt at delvist regenerere adsorptionskapaciteten af kolonnerne ved at pumpe en regenereringsopløsning igennem, som det med succes er blevet demonstreret i denne undersøgelse. Yderligere forskning er imidlertid nødvendig for at verificere de foreløbige resultater, der præsenteres her.

- SCWO har vist sig at være meget effektiv til mineralisering af PFAS-forbindelser uanset medietype, koncentration og type af PFAS-forbindelse. Udover testen dokumenteret i denne rapport, har Aquarden også testet koncentrater fra skumfraktionering og membraner, rå ubehandlet sigevand, koncentrerede brandslukningsskumopløsninger og skylleopløsninger fra GAC-regenerering osv., alle med lignende resultater og destruktions-effektiviteter over 99,99 %. Den primære barriere for implementering i fuldskala er kapacitet og behandlingshastighed.
- Ud over fjernelse af PFAS blev Metalsorb brugt til at undersøge forbehandlingernes evne til at fjerne tungmetaller med henblik på en mulig kombineret fjernelse af både PFAS og tungmetaller. Dette viste sig at være vellykket i et laboratorieeksperiment.
- Fluorescens blev testet som en parameter til at bestemme gennembrud hurtigere end traditionel PFAS-analyse. De foreløbige undersøgelser indikerer, at denne metode kunne anvendes som et supplement til traditionel PFAS-analyse. Yderligere studier bør gennemføres for at videreudvikle metoden.
- Storskala PFAS-behandling på deponier er allerede blevet implementeret på flere skandinaviske deponier. Behandlingen er overkommelig og kan installeres i containere eller et isoleret telt.

1. Introduction

1.1 PFAS

PFAS is a group of over 12,000 synthetic organic fluorine compounds characterized by at least one fully fluorinated carbon atom (OECD 2023). These substances can be designed to repel water or oil and are highly stable. The range of applications is vast, and the substances have been developed and widely used since the 1940s in many different industries (Nicolajsen and Tsitonaki 2016). The high chemical stability of these substances and their extensive use lead to accumulation in the environment.

Accumulation of PFAS combined with concerns about the toxicity of many of these substances, even at low concentrations, has brought them into the public spotlight - in Denmark especially after spring 2021, when high concentrations of PFOS from firefighting foam were found in the meat of nearby grazing cows and in blood of the humans who had consumed the meat. Worldwide, PFAS has become of concern, as e.g., PFOA has been detected in more than 98 % of the U.S citizens in low levels (ppb) (National Center for Biotechnology Information 2023a). PFAS was also found to be carcinogenic in animals and is associated with various human health effects (National Center for Biotechnology Information 2023b). High PFAS concentrations were found in the blood of remote Arctic Inuit, despite being far from PFAS sources. PFAS is transported through water and air, accumulating in marine predators, which are the Inuit's main meat source (Sonne et al. 2023). PFNA and PFOS concentrations were found to be as high as 2 and 3 µg/kg respectively reported in Haddock filet from the Lofoten Islands (Kögel et al. 2021). The Danish Health Authorities have reported indicative increased risk for the development of kidney cancer, increased cholesterol, lower birth weight, and decreased antibody response in connection with vaccination (Sundhedsstyrelsen 2023). The potential toxicity of all PFAS compounds is far from being fully identified, but the European Food Safety Authority (ESFA) has set a current tolerable weekly intake (TWI) of 4,4 ng PFAS/kg body weight (EFSA 2020) and PFOA Relative Potency Factors are estimated (PFOA-RPF) (Scheer, 2022).

An example of a PFAS compound is shown below (FIGURE 1). Each PFAS molecule consists of at least one fully fluorinated carbon atom, which is often only one out of a long chain of such fully fluorinated carbon atoms. This chain constitutes the hydrophobic part of the molecule, whereas a terminal group at one end of the molecule often constitutes a hydrophilic part. This duality is what gives PFAS compounds their unique properties and the very strong carbon fluoride bonds contribute to the difficulty of removing them entirely from the environment.

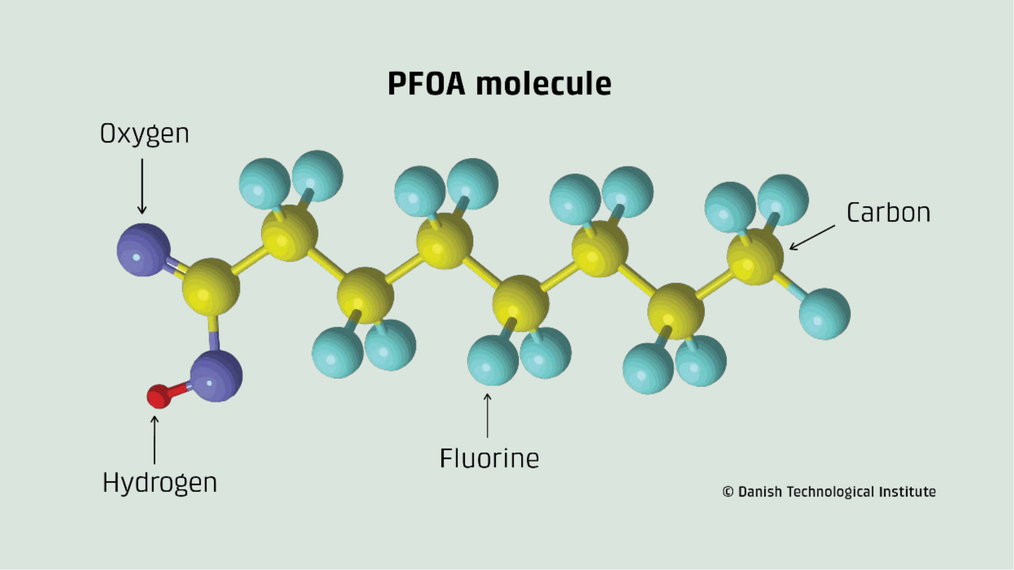


FIGURE 1. Molecular structure of PFOA, one of the many PFAS compounds found in the environment.

1.2 PFAS occurrence in the environment

The use of PFAS in products inevitably releases PFAS into the environment. This occurs both directly from PFAS-production sites, during product use (e.g., firefighting foam, household products), and at the end of product usage by e.g., insufficient incineration or by slow release at landfills (FIGURE 2). PFAS is distributed with water and with wind in aerosols both locally and globally, therefore the use and production of PFAS results in spread to the environment at a global scale. FIGURE 2 highlights the various paths leading to the distribution of PFAS in the environment, as well as how it reenters the food and households, completing the “PFAS cycle”.

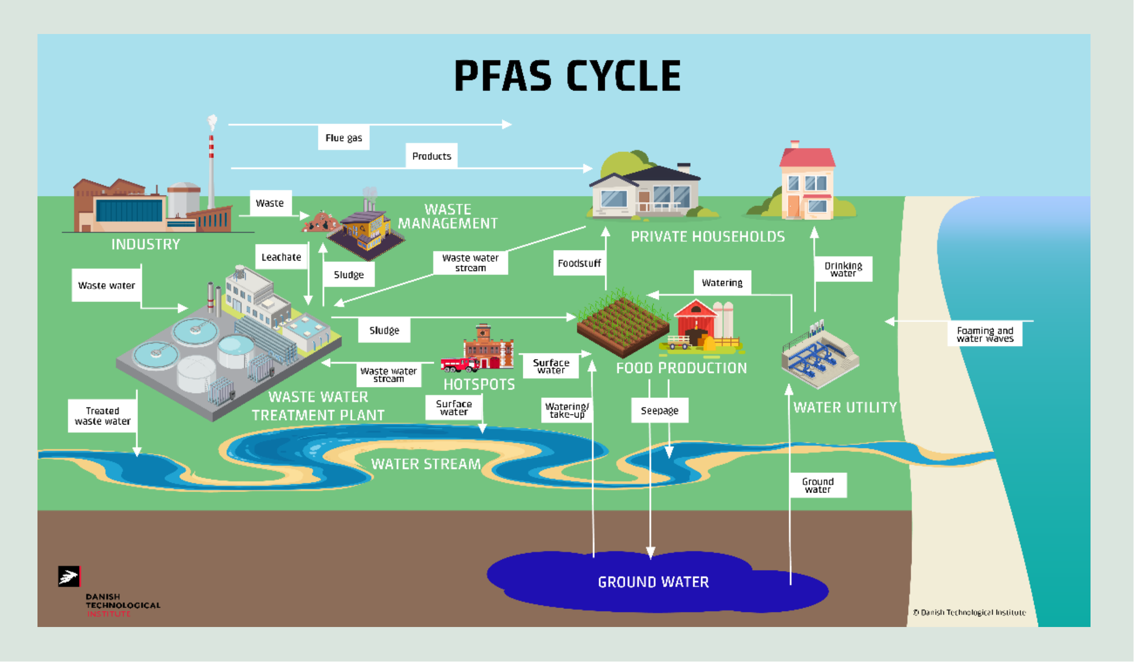


FIGURE 2. Schematic overview of the PFAS cycle in the environment. PFAS from industry is transferred to the environment through products, air, and waste. Treated wastewater containing PFAS seeps through the soil and spreads to various water sources, eventually contaminating ground water and crops for human consumption.

There are several PFAS hotspots in the environment, including historical sites of PFAS production, fire schools where PFAS has been used in firefighting foams, civil and military airports, and landfills containing PFAS-contaminated waste. PFAS-containing products, such as non-stick cookware and stain-resistant textiles, can end up in landfills. As these products degrade, PFAS can leach into groundwater and surface water, creating hotspots near landfill sites. Wastewater treatment facilities can be hotspots due to the presence of PFAS in domestic and industrial wastewater. These compounds can pass through wastewater treatment processes and be released into the recipients (Salvatore et al. 2022).

If PFAS hotspots are not effectively contained or dealt with, there is an imminent risk of contamination spreading to the surrounding environment. However, it has been reported that PFAS is spreading much more extensively, as it has been found as far away as in the arctic environment. (Muir et al. 2019). As PFAS compounds do not completely degrade through any known natural process, effected ecosystems, including soil and water, will remain polluted for extended periods of time. Plants, animals, and microorganisms can consume PFAS from contaminated water or food sources, as well as through air or soil, leading to the accumulation of these chemicals throughout the food chain. This can result in various negative health effects on the organisms involved in the ecosystem including humans (Sundhedsstyrelsen, 2023).

1.3 PFAS removal and destruction

1.3.1 PFAS removal techniques

The process of PFAS elimination can be expensive, thus it is vital to remove PFAS from high-volume sources and concentrate them into smaller volumes before undergoing destruction. It is also crucial to minimize waste streams containing PFAS during pretreatment as much as possible, as these also need to be subjected to destructive methods.

Foam Fractionation

Foam Fractionation (FF) is an efficient technique for eliminating long-chain PFAS from water that tends to form foam. The method involves moving air bubbles through the water, which causes PFAS molecules to accumulate at the interface between the bubbles and the water. These molecules are then transported to the water's surface as foam (Wang et al. 2023). This phenomenon has been observed naturally along the Danish coast where ocean foam contains high concentrations of PFAS (Miljøstyrelsen 2023).

Filtration

The elimination of short-chain PFAS (3-4 CF_2) requires nanofiltration (Malovanyy et al. 2023). However, this technique is not suitable for water matrices with high contamination levels and organic load, due to the filter's vulnerability to clogging. Microfiltration can however be used as a pretreatment step following coagulation/flocculation, to reduce organic content before adsorption.

Adsorption

Adsorption, where molecules or particles from a fluid adhere to the surface of a solid material (adsorbent), has traditionally used activated carbon for PFAS adsorption. Recently, specially designed ion-exchange resins have emerged as a superior alternative for PFAS adsorption. Adsorption techniques are necessary to achieve very low levels of PFAS. The success rate of these techniques relies on low levels of organic matter in the water, which compete with the adsorbents, reducing their ability to bind and effectively remove PFAS. Hence, pretreatment to remove organic matter is a crucial step when using adsorption techniques.

Flocculation

Flocculation using flocculants specifically designed to trap and remove PFAS has emerged as a viable option to remove most of the PFAS contaminants and concentrate them in the sludge.

1.3.2 PFAS destruction

Due to the high stability of the fluor-carbon bond in PFAS substances, extreme conditions are required for complete defluorination, such as 1400°C for the most stable PFAS substances. Therefore, it is crucial to concentrate PFAS before destruction to reduce costs and ensure complete defluorination to prevent PFAS reintroduction into the environment after removal from the original PFAS source. Another emerging method of PFAS destruction is supercritical water oxidation.

High-Temperature Incineration

Incineration is a highly effective method for PFAS destruction. It involves the exposure of PFAS-containing materials to very high temperatures (above 1000°C) in specialized incinerators. At these temperatures, PFAS molecules are broken down into simpler and less hazardous compounds. However, this method requires dedicated facilities and stringent emission controls to prevent the release of harmful byproducts (Meegoda et al. 2022).

Supercritical Water Oxidation

Supercritical water oxidation (SCWO) is a promising technique for PFAS destruction in water matrices. The method uses supercritical water, which exists beyond its critical temperature (374°C) and critical pressure (22.1 MPa), to efficiently oxidize and destroy PFAS molecules. The high temperature and pressure of SCWO conditions promote the breakdown of PFAS molecules through oxidation reactions, resulting in simpler and less toxic byproducts (Krause et al. 2021). The application of this technique is the subject of chapter 8.

The selection of destruction technology depends on several factors, such as the type of PFAS compound, the contaminated medium, and the scale of contamination. The effectiveness of each method varies, and some PFAS compounds may be more resistant to destruction than others. The development of cost-effective and environmentally responsible PFAS destruction technologies is an ongoing area of research and innovation in the field of environmental remediation, including the experiments set up in this project.

1.4 Objective

The objective of the PFAS-inator project was to develop a more economically and environmentally sustainable solution to PFAS removal and destruction from landfill leachate. The destruction part of the project would take its offset in SCWO, a technology that is designed to completely mineralize PFAS. As this technology is costly, the PFAS must be concentrated in as small volumes as possible to be economically and energetically feasible on a larger scale. Therefor the project includes the development of pretreatment and concentration technologies, using a combination of flocculation, sedimentation, membrane filtration, and adsorption technologies. In short, the project aimed to:

- Develop pretreatment technology to remove compounds other than PFAS from landfill leachate, including a wide range of organic compounds to support the efficiency of adsorbents
- Identifying cost-effective adsorbents for the concentration of PFAS
- Select the optimal eluent for effective elution of adsorbed PFAS (regeneration capacity of adsorbents)
- Document the complete destruction of PFAS compounds in various water matrices using SCWO technology.
- Estimate CAPEX and OPEX of a system able to completely pretreat and concentrate PFAS from landfill leachate.

2. PFAS variation in leachate from landfills

Considerable variability is evident in the concentration and composition of PFAS within landfill leachate, as well as in the volume of effluent discharged. This chapter investigates the variability in PFAS concentration and composition in landfill leachate, influenced by factors such as waste composition, landfill practices, landfill age, regional factors, and seasonal weather changes. The section underscores the heterogeneity in PFAS concentration and composition, based on an analysis of leachate samples from five Danish landfill sites. The chapter also explores the fluctuation in landfill effluent volume, using Audebo Miljøcenter as a case study. Influencing factors, including season, precipitation, and landfill management practices, are discussed. The section highlights the challenges faced by Danish landfills lacking buffer tanks, especially during heavy rainfall, and the resulting implications for wastewater treatment plants.

2.1 PFAS concentration and composition variability in landfills

The concentration and composition of PFAS in landfill leachate can vary significantly due to several factors:

- Waste Composition: The types and amounts of PFAS-containing products and waste disposed of in landfills can vary, leading to variations in the concentration and composition of PFAS in the leachate.
- Landfill Practices: Different landfill management practices, such as waste compaction, cover materials, and leachate management systems, can influence the release of PFAS into the leachate. For example, certain cover materials may prevent or reduce the infiltration of rainfall into the landfill, which can affect leachate generation and PFAS concentrations.
- Age of Landfill: Older landfills that received waste may contain higher concentrations of these substances compared to newer landfills, although older landfills without cover will have reduced PFAS concentrations due to ongoing wash out.
- Regional Factors: The concentration and composition of PFAS in landfill leachate can also be influenced by regional factors such as industrial activities, disposal practices, and the presence of specific PFAS-containing products in a particular area.
- Seasonal fluctuations in weather: Heavy rainfall, drought, or freezing temperatures influence the concentration and volume of leachate to be handled in various seasons.

Leachate samples obtained from five distinct landfill sites in Denmark were subjected to analysis, revealing significant heterogeneity in both the concentration and composition of PFAS (FIGURE 3 and FIGURE 4).

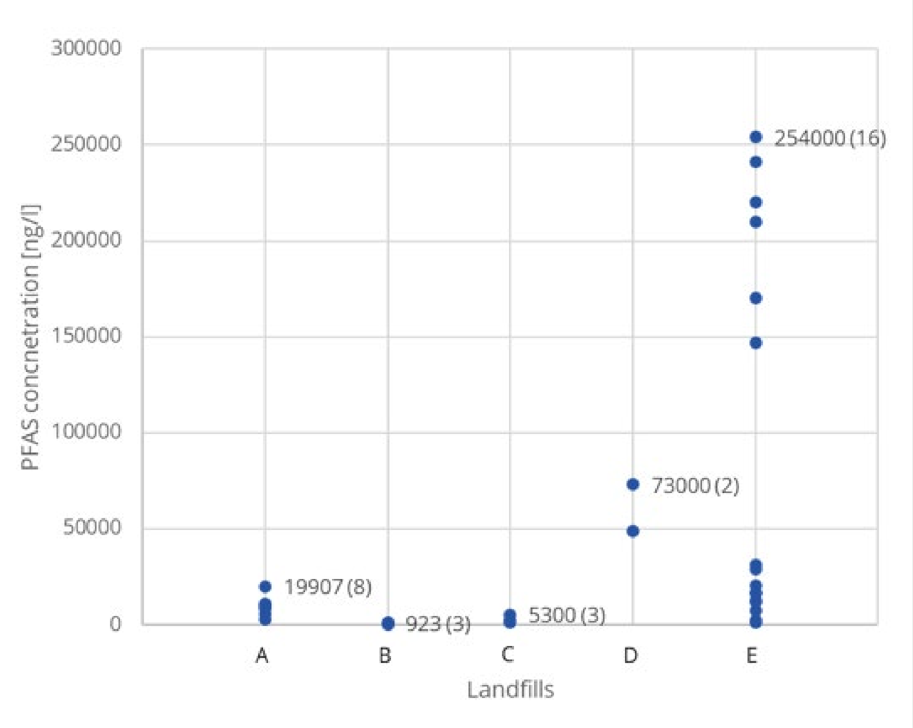


FIGURE 3. PFAS content in landfill leachate from 5 different landfills. Grab samples from different cells and times. The numbers are the highest concentration measured at the landfill, and the numbers in brackets represent the number of samples analyzed per landfill. PFAS sum 12 was analyzed for landfill A-D, and sum 22 was analyzed for landfill E.

The concentrations of PFAS vary significantly between and within landfills, as well as over time. At landfill E, mineral waste, ash, and shredded asbestos account for the lowest PFAS concentrations observed, and there is a correlation between higher PFAS concentrations and newer cells.

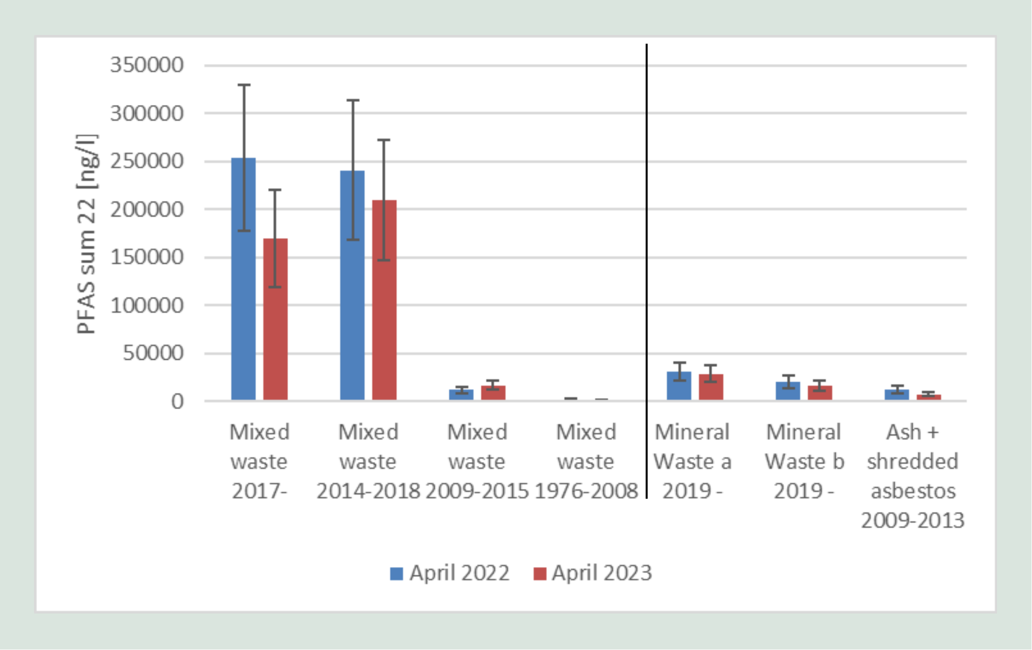


FIGURE 4. PFAS concentrations were analyzed from different landfill cells of landfill E. The error bars represent the analysis uncertainty. If there is no end date specified, it denotes that the cells are currently active.

It is still too early to conclude the extent of the impact of leaching effects on the data, given the limited available data on the decrease of PFAS over time and the unknown composition of waste deposited (mixed waste). Nevertheless, the elevated concentration of PFAS in the leachate indicates an ongoing leaching process occurring in Danish landfills, which remains uncovered. Uncovered landfills will slowly have their PFAS leached to the environment, lowering the concentration at the older deposits. In contrast, most other countries like Norway and Sweden employ a different strategy by covering their landfills, thereby limiting leaching. This strategy aims to retain as much as possible in the landfill, rather than washing all the pollutants out gradually. Initially, it was believed that pollutants would be washed out after 30 years, but data from a landfill in Hvalsø still showed elevated concentrations (1500-3000 ng/l), for example, the closed even 30 years after closure.

The composition of PFAS varies significantly across different landfills, as depicted in FIGURE 5, showing the percentage composition of PFAS in the cell with the highest PFAS concentration for each landfill (remark: analysis has not been conducted on every cell across all landfills).

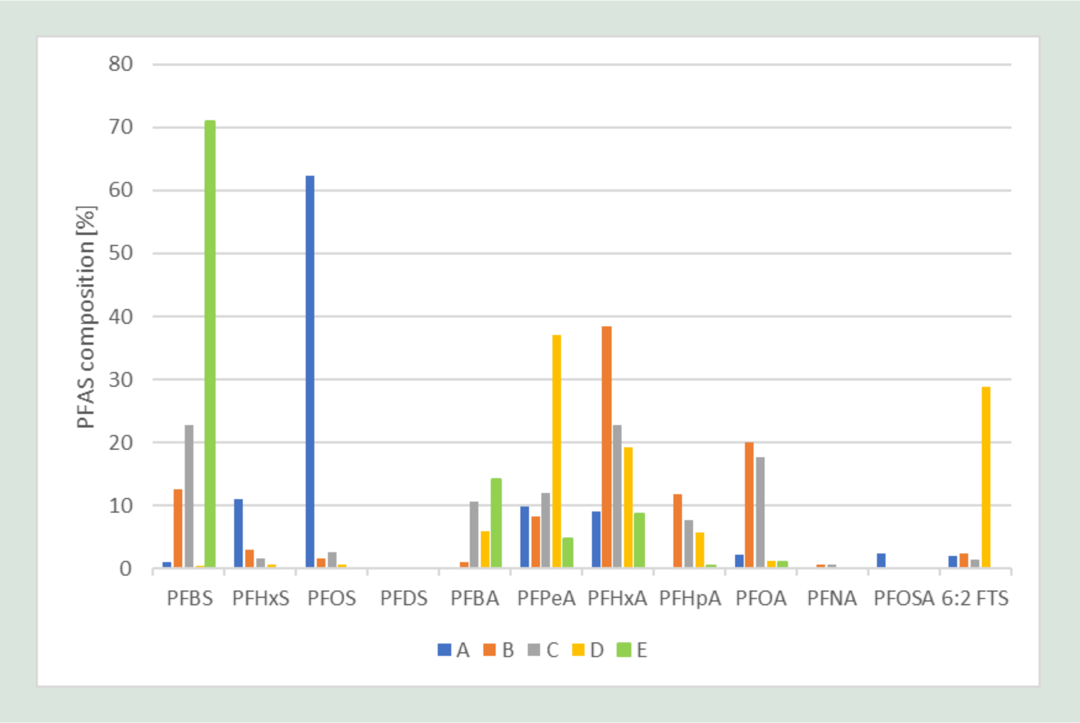


FIGURE 5. PFAS composition in % for the cell with the highest total PFAS concentration at each landfill A - E.

Some landfills exhibit a scenario where a single PFAS substance predominates, requiring specific and targeted actions to identify the precise point source responsible for the discharge of PFAS. These measures are necessary to effectively implement interventions that halt the release of PFAS contaminants into the environment. Conversely, other landfills exhibit a more diverse pattern of PFAS substances, indicating a potentially extensive range of sources.

2.2 Effluent volume variations in a landfill

The fluctuation of leachate volume generated at Audebo Miljøcenter is illustrated in FIGURE 6.

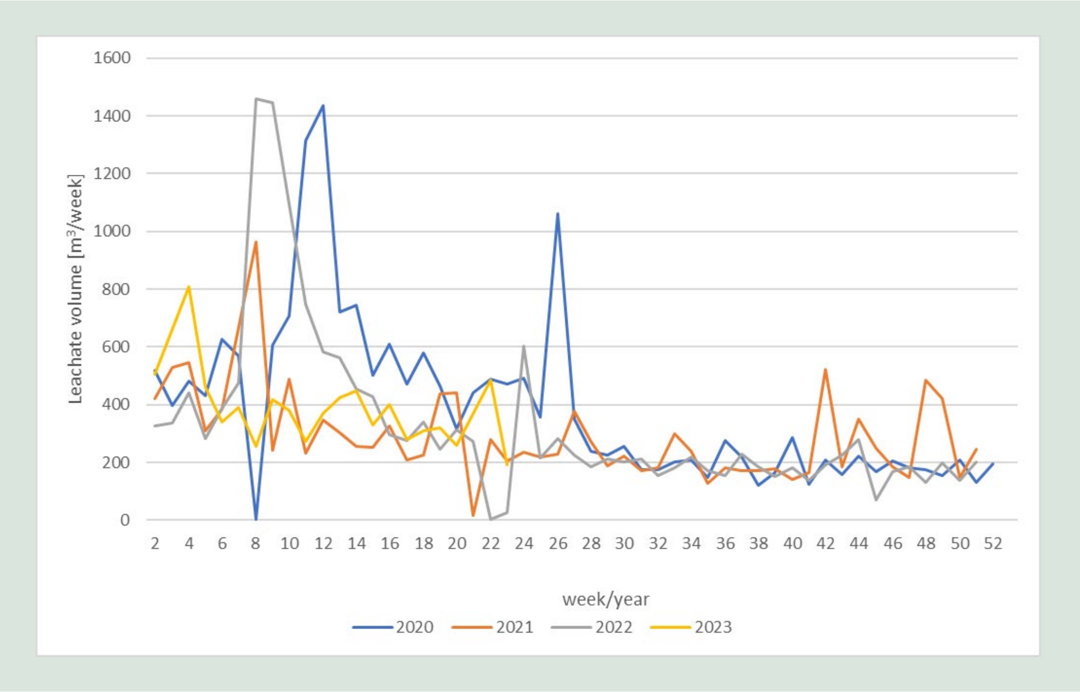


FIGURE 6. Effluent volume of leachate from Audebo Miljøcenter 2020-2023.

The effluent from landfills can vary, primarily influenced by factors such as season and precipitation, but landfill management practices also play a role.

These variations in effluent volume can further contribute to the variability observed in PFAS concentrations in landfill leachate, but also to the concentration of many other compounds.

In Denmark, several landfills lack buffer tanks to accommodate heavy rainfall events, posing challenges for the subsequent municipal wastewater treatment plants. As a result, during rainy seasons, these treatment plants increasingly restrict the acceptance of leachate, shifting the burden onto the landfills. Consequently, the implementation of buffer tanks at the landfills becomes more prevalent to address this issue. In periods of less rainfall, the municipal wastewater treatment plants would then have to accept larger volumes of water to get rid of the leachate accumulated in the buffer tanks during the rainfall events at the landfill.

3. Organic content – a key factor for PFAS removal efficiency

The efficiency of PFAS removal on adsorption columns is influenced by the organic content, as it competes with PFAS for binding sites on the adsorption material. Therefore, it is necessary to remove organic matter as much as possible to extend the lifespan of the adsorption columns.

Landfill leachate contains a significantly higher concentration of organic matter compared to PFAS. It is worth noting though that both the organic matter and PFAS concentrations in landfill leachate vary significantly over time and across different locations.

The organic matter is derived from the biodegradation of natural organic matter, as well as various synthetic chemicals and polymers that have been deposited at the landfill over time. The variability in the organic content of the leachate is influenced by several factors such as variation in rainfall and temperature which influence the leaching as well as the biological activity of degraders in the landfill. Additionally, water levels and flow in the landfill influence the leachate as many landfills are very heterogeneous in their deposited material. There is even greater variation observed among different landfills, which can be attributed to the diverse sources of deposited materials and the varying management practices implemented over time. These factors contribute to significant differences in the composition and characteristics of landfill leachate between different sites.

The presence of organic compounds in water takes up sites on filter material and thereby reduces the ability of the filter materials to adsorb PFAS effectively. Therefore, pretreatment of landfill leachate becomes crucial to enhance the efficiency of PFAS removal during the cleaning process. The interference of organic matter with PFAS sorption is attributed to several mechanisms. These include competition for sorption sites, primarily in ion exchange processes, the general sorption of larger molecules onto the surface of sorbents, which hinders access to active sorption sites, and the growth of biofilms on the sorbent material, reducing contact between the water and the sorbent material within the column. These mechanisms collectively contribute to decreased efficiency in PFAS sorption when organic matter is present.

Due to the various negative interaction mechanisms, any presence of organic matter is undesirable when treating landfill leachate. Therefore, pretreatment of leachate can be guided by simple parameters such as Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC), without significant concern for the specific quality of the organic matter.

3.1 Variability of organic content in leachate effluent from landfills

The concentration and variability of organic contents among the cells and the leachate buffer tank at Audebo Miljøcenter are illustrated in FIGURE 7.

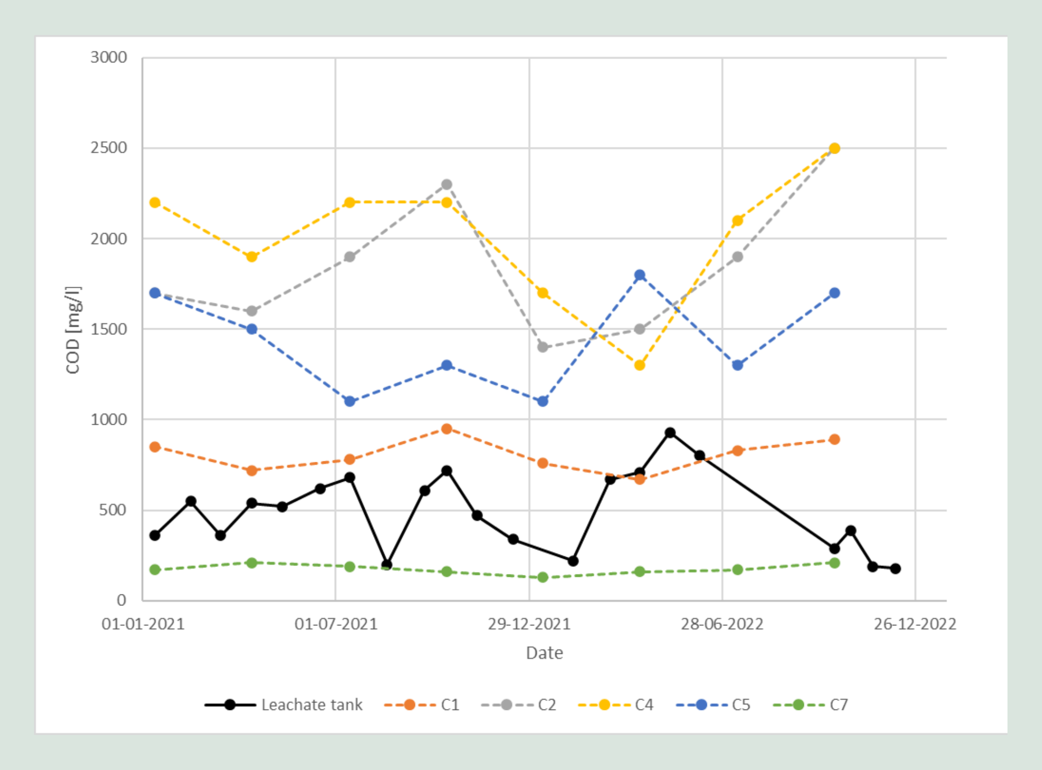


FIGURE 7. Concentration of organic matter measured as COD of 24-hour samples in cells 1 to 7 and leachate buffer tank (mix of cells 1-7) at Miljøcenter Audebo, Denmark. Cells 1-4 are closed cells with mixed waste, cell 5 is an active cell with mixed waste, and cell 7 is an active cell with primarily asbestos waste (eternit plates) and remnants of soil and wood from fire sites. The volume of the leachate load is unknown.

FIGURE 7 illustrates the variation of organic matter in different cells at different timepoints. The large variation in COD is challenging for the treatment of the leachate.

The COD concentration delivered to the buffer tank shows sudden variations due to the pumping strategies employed.

3.2 Organic load versus PFAS breakthrough

When treating PFAS-contaminated water, one well-known technology is the adsorption of PFAS on activated carbon or ion exchange resins. The organic carbon, however, competes for the binding sites, making the organic carbon load in the water crucial for the adsorption capacity. Adsorption capacity is often measured in the number of bed volumes before break-through of a defined maximum of PFAS in the outlet.

The effect of organic carbon in leachate on the removal efficiency of various PFAS substances was tested in a laboratory test. Raw, flotated, and ozonated leachate was treated using ion exchange resin columns subject to 8.000 bed volumes of leachate, during which PFAS concentration in the outlet water was monitored. In FIGURE 8 the number of bed volumes before identified break-through and full break-through (100% of inlet concentration measured in the outlet) is provided for each PFAS detected in the leachate. The breakthrough curves for leachate treated with ozone resulted in COD values between those of untreated and flotated leachate (results not shown).

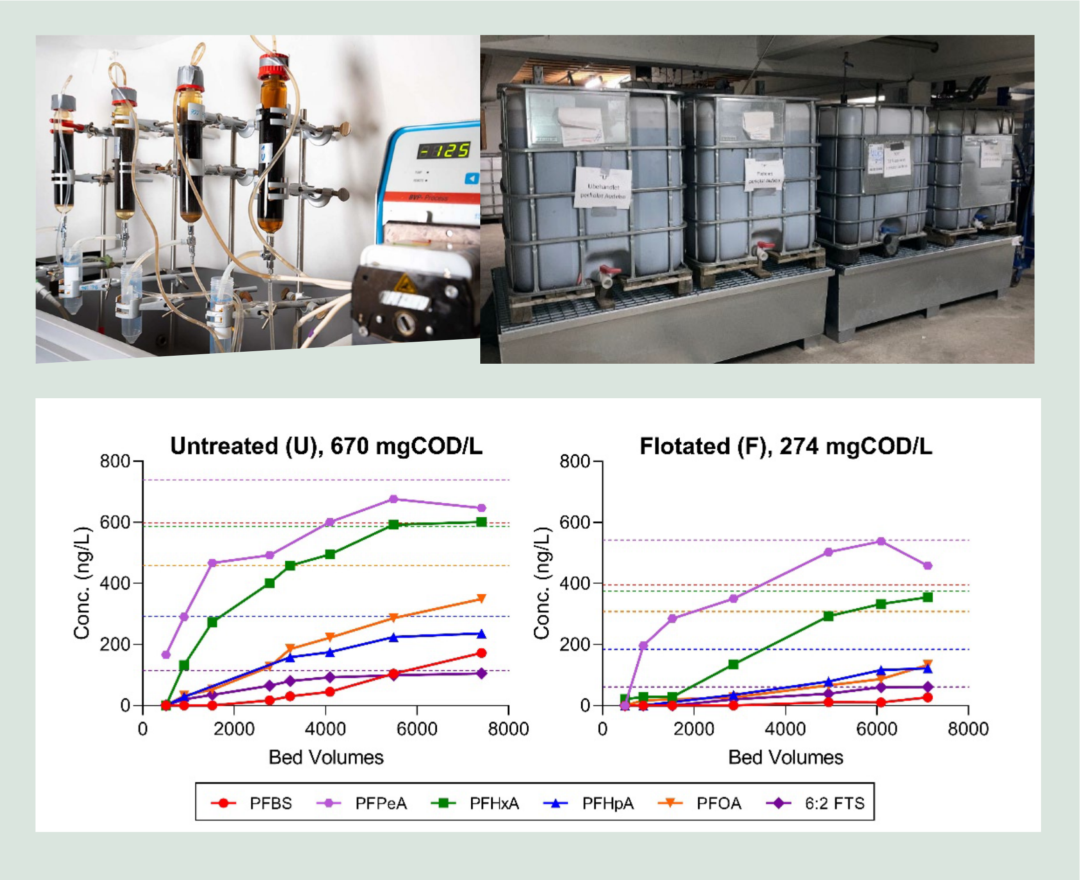


FIGURE 8. Breakthrough behavior of different PFAS on resin columns dependent on the organic content. The dotted lines represent the inlet concentration.

Note from FIGURE 8 that the volume of inlet leachate before break-through of PFAS is dependent both on the specific PFAS substance and the concentration of organic carbon. The lower the COD (leachate treated with flotation) the larger the volume of inlet water before break-through, and longer sulfonic acid type PFAS break-through later than shorter carboxylic acid type PFAS.

One major cost factor in the removal of PFAS from leachate is the ion-exchange resin, which includes the production of the resin, the labor required for replacing used resin, and the disposal of the spent resin. Therefore, there is significant potential to enhance PFAS removal efficiency by first removing organic carbon before adsorbing PFAS. Removal of COD in this report is referred to as “pretreatment”.

3.3 Organic load versus fluorescence breakthrough

Fluorescence intensity identifies the presence and the amount of specific molecules in a medium. It might be possible to correlate the breakthrough of natural fluorescensing organic matter with various chain-length PFAS and use this to predict the loss of absorption capacity for PFASes which can be used to guide the control sampling and replacement of sorption materials. Four different fluorescence components ranging from 220 to 400 nm of Excitation wavelength and 310 to 480 nm of Emission wavelength were investigated to understand the impact of the pretreatment process on the changes in fluorescence over the breakthrough experiment (Sciscenko et al., 2022).

Among all the pretreatment processes, leachate pretreated with flotation has shown it be an efficient way to delay the breakthrough of the intensity of four studied fluorescence components

(FIGURE 9). For example, the breakthrough of peak A in the leachate pretreated with 50% ozonated and 100% ozonated are observed at bed volumes of approximately 8000 and 3000 respectively, while no breakthrough was found yet for flotation.

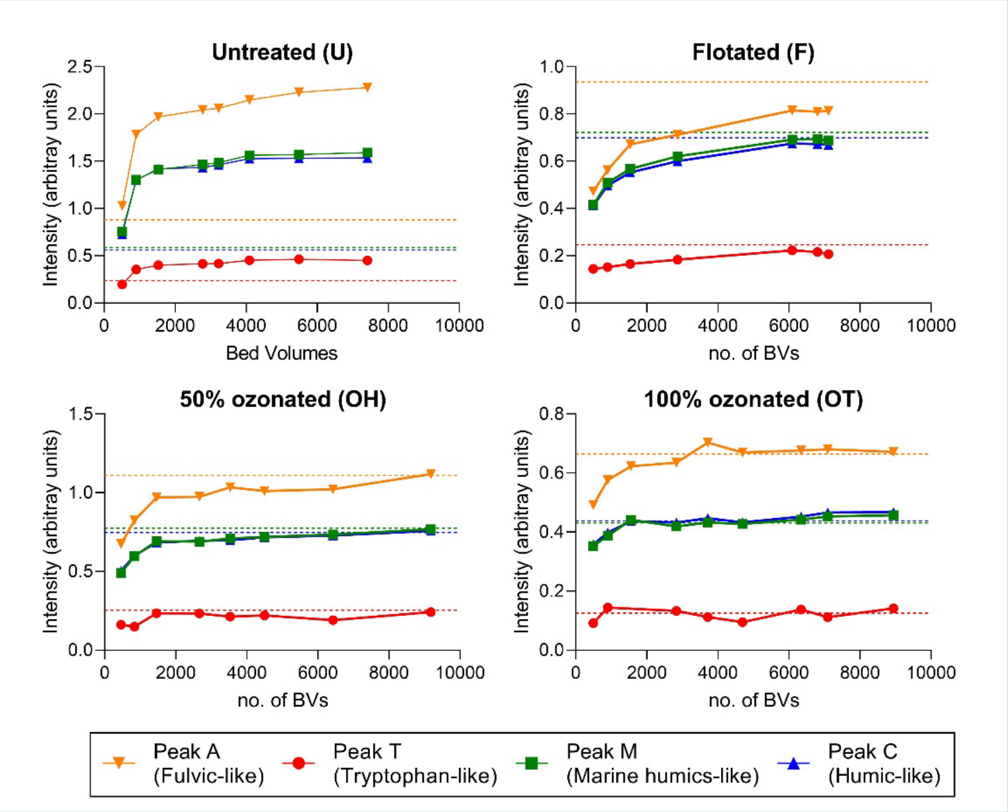


FIGURE 9. Breakthrough behavior of different fluorescence components on resin columns dependent on the organic content. The dotted lines represent the inlet concentration.

3.4 Pretreatment effect on COD removal

Leachate in the young phase contains a high concentration of volatile fatty acids that are easily biodegradable, however, a high concentration of humic-like substances, which are non-biodegradable are found in the stabilized phase of leachate (Kurniawan et al., 2006). The purpose of pretreatment is to remove as much organic carbon as possible. There is a tradeoff between spending high amounts of energy and chemicals and creating large amounts of organic waste and removing organic carbon for improved adsorption capacity. Various pretreatment technologies focusing on organic carbon removal were tested in laboratory setups both alone and in combination at two different landfills. The results are summarized in FIGURE 10. Coagulation–flocculation has been employed for the removal of non-biodegradable organic compounds and heavy metals from landfill leachate. Due to its inherent physical properties, large surface area, and high adsorption capacity, adsorption using powdered activated carbon (PAC) has been receiving considerable attention recently for the removal of organic and inorganic pollutants from contaminated wastewater.

Using a range of pretreatment methods alone or in combination, it was possible to achieve between 0 and 70% removal of organic material, with most experiments achieving less than 50% removal (FIGURE 10). A high variation between leachates indicates that carbon removal is to be optimized for each water type.

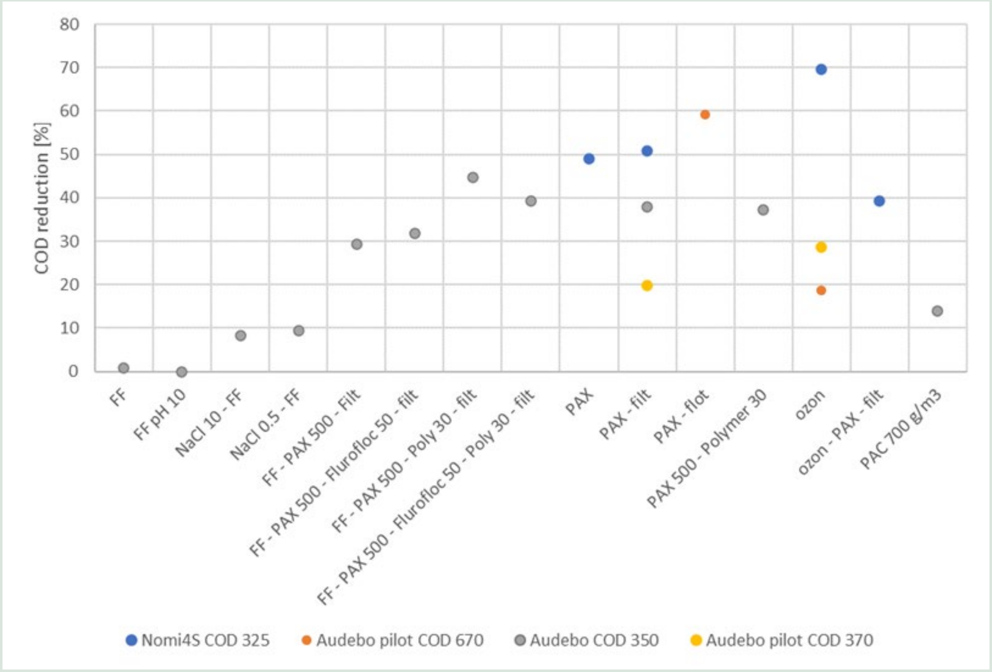


FIGURE 10. Effect of various combinations of pretreatment technologies on different leachate types (different colors). FF = foam fractionation, flot = flotation, filt = filtration, ozon = ozonation, NaCl [mM], PAX [ml/m3], Pol = Polymer [ml/m3], Fluorfloc [mg/l], PAC = powder activated carbon jar experiments unless otherwise specified (Pilot = 1 m^3).

4. PFAS removal from leachate

As the destruction of PFAS-contaminated material is expensive and resource-consuming, concentrating the waste stream as much as possible is preferrable. This is achieved either through a specially designed PFAS-targeting flocculation chemical or through adsorption to a material such as GAC or resin. Both techniques were illustrated successfully in lab, pilot- and full-scale experiments. Resins have been determined to outperform GAC when it comes to adsorption capability. Preliminary experiments illustrated the possibility of regenerating the adsorption capacity of both GAC and resins, which is a promising next step in reducing the environmental footprint of PFAS treatment technologies.

4.1 General remarks on PFAS removal

As described in the previous sections leachate is a complex mixture containing many different compounds and also high amounts of very recalcitrant organics. It is possible to degrade the PFAS in the water using e.g. SCWO, but the price and energy consumption of doing this are very high. There is therefore a need for technologies that can concentrate the PFAS prior to destruction. As previously described several techniques exist for up-concentration, with each their drawback. All data suggest that the only techniques that can ensure even very low discharge levels are ion exchange and adsorption, but both are highly affected by the presence of organic material in the water. Organic content has to be removed as well as possible if adsorption is a necessary step.

4.2 PFAS removal by adsorption

Adsorption technologies are among the most common for PFAS removal from liquid medium. The liquid is pumped through a packed column of adsorbent material, which removes the PFAS and lets clean water out of the other end. Common adsorption materials include GAC and ion-exchange resins. GAC is a cost-effective adsorbent extensively utilized for the removal of micropollutants, from water, but is not an effective adsorbent for PFAS. The limited effectiveness of GAC necessitates the use of alternative adsorption materials. Among these, specially designed ion exchange resins have emerged as an effective option.

The versatility in adsorption of both GAC and resin materials makes them great in different applications but is a problem when the purpose is to adsorb specific compounds such as PFAS. The leachate water not only contains PFAS but also a range of other organic compounds, which compete with PFAS for space on the adsorption columns. As such, pretreatment of the leachate to remove excess organic material is a necessary step to extend the effective lifespan of the material. This is especially true when the leachate contains organic material in concentrations several magnitudes higher than PFAS, which is often the case.

The adsorption capacity for PFAS-removal was tested in isotherm laboratory experiments, in pilot plant setups, evaluating various adsorption (new and regenerated) material and as an effect of various pretreatments (section 4.3).

4.2.1 Laboratory adsorption experiment

To characterize the sorption property of the Pyrolite resin sorption isotherms were made in clean water which quantified the sorption capacity of the resin and the equilibrium between low water concentrations and concentrations in the sorbent which are basic parameters for designing sorption in columns. Additionally, since resins have previously mostly been used for removing PFAS'es from relatively clean water intended for water supply, the effect of the matrix in percolate water was investigated in a batch experiment.

FIGURE 11. Experiment with Pyrolite (Left) was made in Falcon tubes (middle) and HDPE plastic ware flasks (right) which adsorb PFAS'es less than laboratory glass.

Different dosages of ion exchange resins (Pyrolite PFA694E) were weighted out and added into the plastic tube with 30 mL of tap water spiked with different initial concentrations of PFAS. Positive control (only including PFAS) and negative control (only including ion exchange resin) were also introduced during the adsorption experiment. The plastic tubes were placed on the shaker and incubated for 24 hours under 76 rpm.

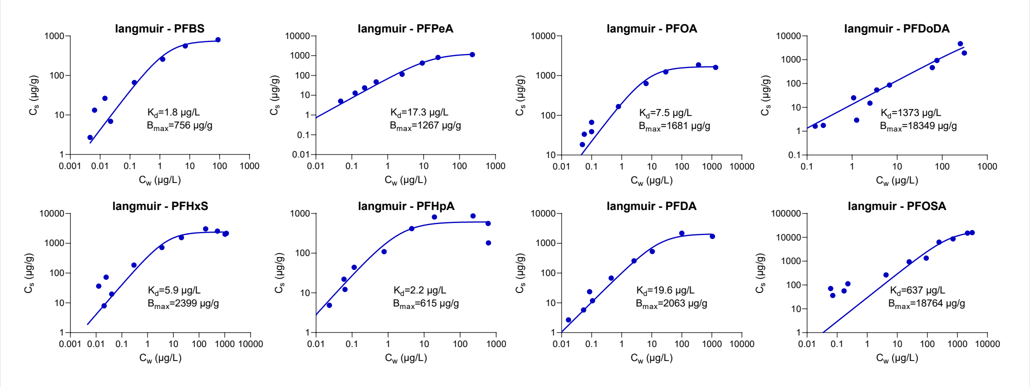


FIGURE 12. Sorption isotherms for 9 PFASes in drinking water for Purolite resin.

The sorption isotherms in FIGURE 12 illustrate the relation between equilibrium concentrations in the water phase (Cw) and sorbed phase (Cs) which is linear at lower concentrations but as the sorption capacity is approached the water concentration increases without further increase in the concentration in the sorbent. For the longer-chain PFAS, the adsorption capacity is larger than for the short-chain PFAS.

Besides sorption isotherms for PFAS in tap water, the sorption was also tested in a leachate matrix with different pre-treatments as shown in FIGURE 13 and FIGURE 14. FIGURE 13 illustrates the strong deviation from the sorption isotherms caused by the dissolved matter in the leachate with little remediation effect of the pre-treatments. FIGURE 14 shows for the same experiments the matrix effect on the equilibrium concentration in water which is almost not reduced for the already less well-sorbed PFPeA and 6:2 FTS. From this, it is clear more targeted pre-treatments are needed for very heavy matrixes for an efficient use of ion exchangers such as Pyrolite.

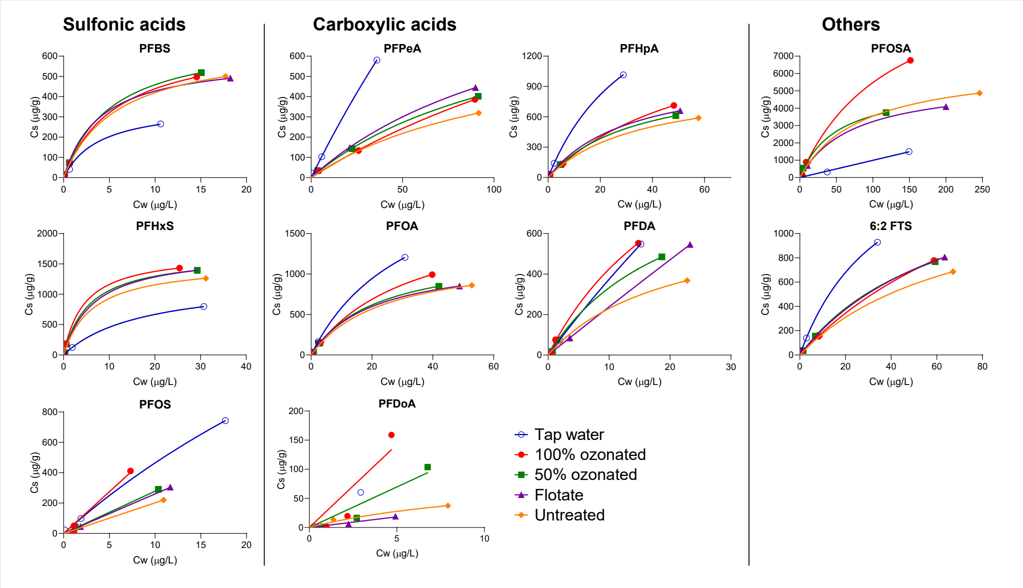


FIGURE 13. Sorption equilibrium of PFAS'es in four variations of leachate with different pretreatment compared to sorption isotherms (blue lines) determined in tap water (from FIGURE 12). The 4 variants of leachate waters are red circle, green rectangle, purple triangle, and orange diamond.

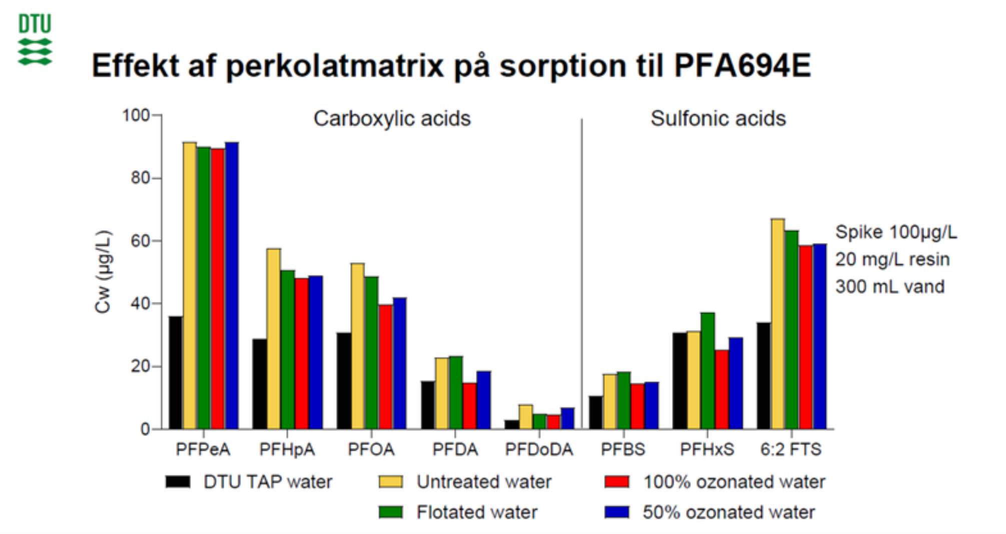


FIGURE 14. Effect of leachate matrix with various pre-treatments on equilibrium water concentrations of selected PFAS'es.

4.2.2 Pilot scale adsorption experiments at Perpetuum landfill (Norway)

A large pilot with pretreatment consistent with coagulation with alumina chloride followed by a ceramic membrane system was operated for 6 months in Northern Norway, see FIGURE 15.

FIGURE 15. Pilot scale test facility at a site in Norway.

This system was used as input for several tests with resin, GAC, regeneration, and even different types of resins. The system was operated in the following configuration:

1. Coagulation with alumina chloride
2. A separation tank where larger flocs were extracted from the bottom
3. Ceramic membrane setup with Cembranes ceramic membrane modules (5 modules of 6,9 m^2 each)
4. Either GAC or resin as a polishing step

The membrane system was operated at a fixed flow of 1,1 m^3/h flow and was backwashed using permeate every hour. The system is operated by a PLC and runs as a standalone unit for the entire testing period. During the 5,5 months of continuous operation, the system was chemically cleaned 3 times, two times using acid and one time using hypochlorite. Cleaning was initiated when trans-membrane pressure reached -0.3 bar. The picture below shows the water from inside the membrane tank and the permeate.

FIGURE 16. Raw leachate (left) and pretreated leachate (right).

In one experiment four small parallel columns of resin and four parallel columns of GAC were set up to test the difference in adsorption capacity given different treatments of both resin and GAC columns. 6 columns were hooked up to the tank for treated water after the membrane setup, whereas 2 columns were connected directly to the untreated water, to compare the effect of pretreatment. The column experiments lasted for approximately 6 weeks, after which all column experiments were terminated, regardless of the remaining adsorption capacity. As such, some columns might have had the capacity for further PFAS adsorption, even though all columns had breakthroughs of PFAS to some extent, at the end of the experimental period. The columns were set up as indicated in TABLE 1 and illustrated in FIGURE 17.

TABLE 1. The difference in setup between columns one through eight.

Column number	Column material	Treatment	Water pretreatment
1	Resin	New	Yes
2	Resin	Regenerated	Yes
3	Resin	Used	Yes
4	Resin	New	No
5	GAC	New	Yes
6	GAC	Regenerated	Yes
7	GAC	Used	Yes
8	GAC	New	No

The regenerated material was produced by running a regeneration solution through a column packed with either resin or GAC, to regain some of the lost adsorption capacity. Columns four and eight contained new column material, the difference being the input water. Columns three and seven were used as benchmarks, to evaluate the improvement in each of the other treatments compared to used column material.

FIGURE 17. Columns one through eight during setup. Water is pumped in at the top and flows out through the bottom of each column.

For each of the eight columns, samples were taken from the outlet at different time points during the one-month experiment period. The samples were analyzed for 14 different PFAS compounds, the sum of which is summarized in FIGURE 18 and FIGURE 20.

4.2.2.1 Resin

The resin columns each contained 100mL of resin and were operated for a maximum of approximately 7,300 bed volumes. The column containing regenerated resin and the column containing new resin fed with water without pretreatment were both terminated prior to the end of the experimental period, due to the clogging of the column material to a degree that no longer allowed water to pass through. The accumulation of particulate material in column four is also evident in FIGURE 19, illustrating the coloring occurring when the water is not pretreated.

It is evident from FIGURE 18 that the new resin has the capacity to adsorb PFAS compounds for a longer period than the other resin treatments. The regenerated resin also shows a partial regain in adsorption capacity when compared to the used resin column. It however does not reach the performance of new resins. This indicates the potential of regeneration to extend the life of resins as a column material, reducing the need for the production of virgin resin material. The results should be seen as preliminary but indicate that regeneration can be a viable solution for resins. Comparing columns four and one makes it evident that pretreatment has a profound positive influence on the longevity of the resin column material. The outlet concentration from the pretreated column at 7500 BV was lower than the outlet concentration of the column without pretreatment at 3500 BV (FIGURE 18), indicating that the lifetime expectancy of the resins is more than doubled using ceramic membranes in combination with coagulation as pretreatment.

Each of the resin columns has a good ability to withstand peaks in inlet concentration, as can be seen when the PFAS in the inlet spikes between 2,000 and 4,000 bed volumes, but the outlet concentrations do not. This is a contrast to the results achieved with the GAC columns, which are not as able to handle spikes in inlet concentration (FIGURE 20).

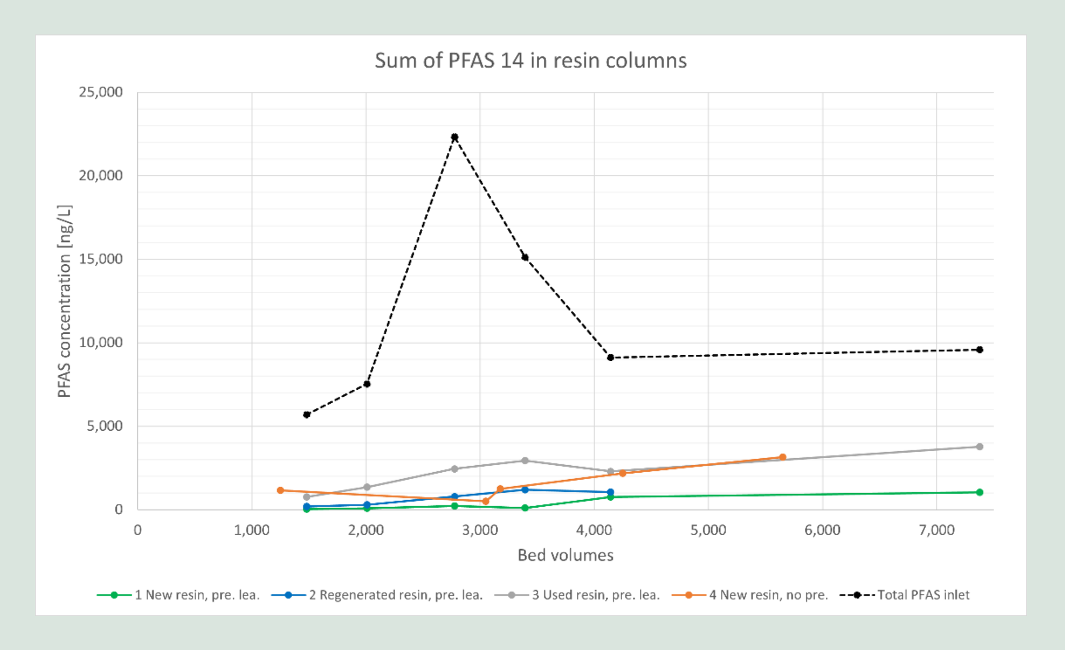


FIGURE 18. Total PFAS concentration in inlet water as well as outlet of the four resin columns, as a function of bed volumes. The PFAS compounds analyzed were 6:2 FTS, PFBS, PFPeA, PFHxA, PFHxS, PFHpA, PFOA, PFOS, PFOSA, PFDA, PFNA, PFDoA, PFTrDA, and PFTeDA. pre. lea.: Pretreated leachate, no pre.: no pretreatment of leachate.

The fourteen different PFAS compounds analyzed were not present in equal concentrations. The main PFAS compound across the experiment was PFOS, which is also the main contributing factor to the peak in concentration between 2,000 and 4,000 bed volumes (appendix 1.1). From the figures it is also possible to conclude that PFPeA, PFHpA, and PFOSA break through the columns first, independent of column treatment. This fits well with what has been experienced elsewhere, the acid group and the chain length determine the efficiency of the ion exchange process.

FIGURE 19. The four resin columns following one day of running. The column material in column four got increasingly darker as the experiment progressed.

4.2.2.2 GAC

The GAC columns each contained 400mL of GAC and were operated for a maximum of approximately 3,400 bed volumes. Column eight containing new GAC and fed with untreated water was terminated after approximately 2,000 bed volumes, due to clogging of the column material. Due to the dark nature of the GAC column material, it is difficult to spot the build-up of organic material in the columns leading to coloration of the column material. The coloration occurring due to non-pretreated water can therefore best be appreciated in resin column 4 (FIGURE 19).

Columns seven and eight, containing used GAC and new GAC without water pretreatment, exhibit almost immediate breakthrough of PFAS (FIGURE 20). The new and regenerated GAC can achieve near 100% removal of PFAS for approximately 1,000 bed volumes, and following 1,800, the capacity of the new GAC is comparable to the used GAC material. The very rapid breakthrough of the non-pretreatment water indicates that GAC as a stand-alone solution would not be a viable solution for this water, especially as the GAC also clogged up very rapidly.

The regenerated column material retains a better removal efficiency than all other GAC treatments past 1,000 bed volumes. This indicates that the regeneration of GAC material might be a viable option compared to simply using new column material every time the capacity of the old material is depleted. This however requires further research, to determine the best regeneration solution, as well as limiting the volume of solution needed for sufficient regeneration. In this experiment, 12 bed volumes of regeneration solution were used, so a distillation step would be required.

Even though regeneration of the GAC material proved successful in this preliminary study, it is evident that resin has a much higher adsorption capacity for PFAS than GAC (FIGURE 18 and FIGURE 20). Given the same inlet concentrations of PFAS, the new resin achieved nearly

100% removal efficiency for 3,500 bed volumes, whereas the new GAC achieved 1,000 bed volumes. The new resins still performed remarkably better than the used resins following 7,300 bed volumes, whereas the new GAC has a similar performance to the used GAC following 1,800 bed volumes.

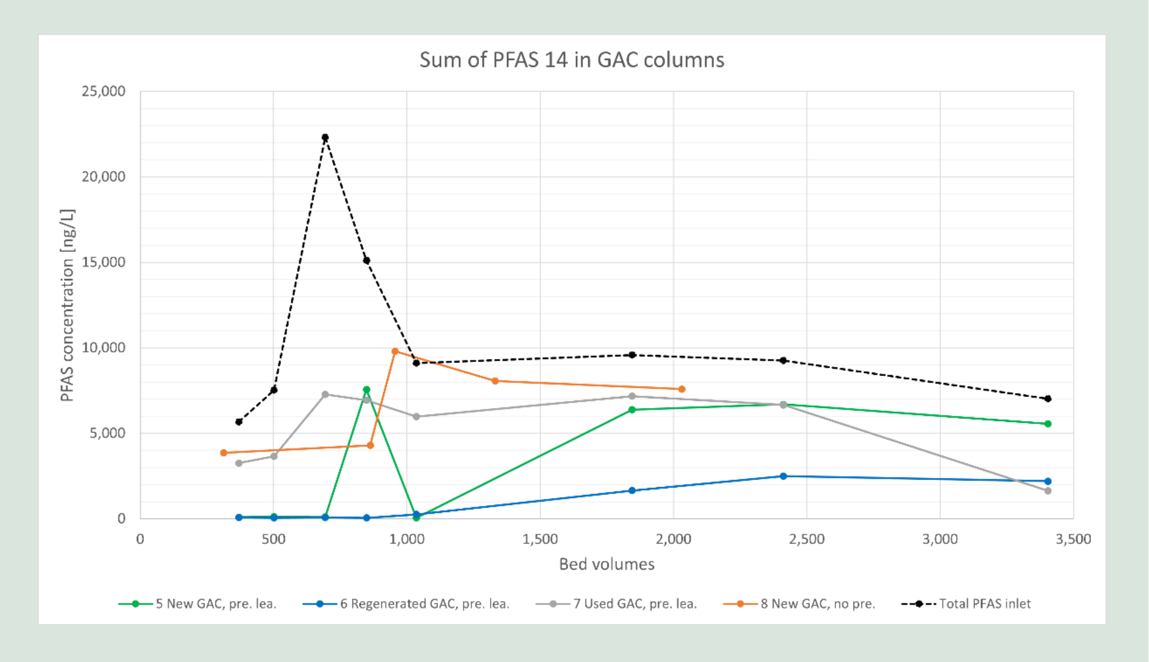


FIGURE 20. Total PFAS concentration in inlet water as well as outlet of the four GAC columns, as a function of bed volumes. The PFAS compounds analyzed were 6:2 FTS, PFBS, PFPeA, PFHxA, PFHxS, PFHpA, PFOA, PFOS, PFOSA, PFDA, PFNA, PFDoA, PFTrDA, and PFTeDA. pre. lea.: pretreated leachate, no pre.: no pretreatment of leachate.

4.2.3 Regeneration potential for adsorption material at Perpetuum landfill (Norway)

The on-site test was conducted to evaluate the regeneration potential of ion-exchange resins as well as activated carbon. The objective was to determine if these column materials could be effectively regenerated and regain their PFAS adsorption capabilities. During the test, the ion exchange resins and activated carbon were subjected to a regeneration process, which involved treating them with a specific regeneration solution to remove the accumulated contaminants and restore their capacity (FIGURE 21).

The results of the test did not yield conclusive evidence regarding their regeneration capabilities but did indicate the potential of regeneration to regain some of the capacity of the activated carbon. As such, this would be an interesting path for future research into regeneration solutions. It is clear that additional research is necessary to better understand the factors influencing regeneration efficiency, optimize regeneration techniques, and identify the most effective regeneration solutions for different types of column materials.

Further studies could explore various parameters, such as regeneration time, concentration of regeneration solution, temperature, and pH, to determine their impact on the regeneration process. Additionally, investigating the effects of different regeneration cycles and the long-term stability of regenerated column materials would contribute to a more comprehensive understanding of their regeneration potential.

FIGURE 21. Column containing used resin material before (left) and after (right) regeneration. The solution visually removes much of the organic material, and to some degree restores the adsorption capacity of the columns.

4.2.4 Full-scale resin column experiments at Perpetuum landfill (Norway)

In addition to the small resin and GAC columns, two large columns each containing 50L of resin, were set up at Perpetuum (FIGURE 22). The first campaign was used to evaluate the difference in performance between two identical columns of the same resin type. The performance was confirmed to be similar (data not shown).

FIGURE 22. A parallel full-scale column set up containing ion-exchange resins. Experiments were conducted at Perpetuum landfill (Norway).

At the end of the first round of resin experiments, the used resin material was removed from each of the columns and cleaned with water. There was a clear visual difference between the resins at the start and end of the experimental period (FIGURE 23). It is evident that organic material accumulates on the resin material over time, contributing to the loss of PFAS adsorption capacity. It was however realized that there had been a small breach in between two membrane modules, leading to a little water flowing around the membrane setup. This was fixed between this experiment and the subsequent test. After this had been fixed the resin looked almost like new even after weeks of operation (section 4.2.2), further highlighting the importance of pre-treatment.

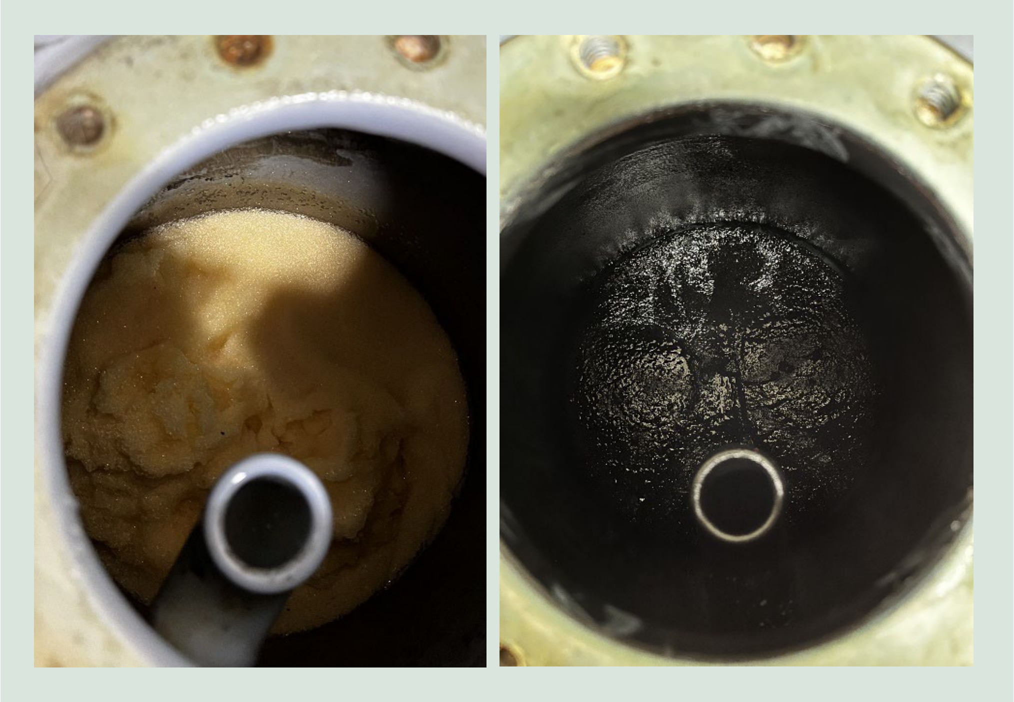


FIGURE 23. Resin before (left) and after (right) full-scale experiments at Perpetuum landfill (Norway).

The second round of full-scale resin column experiments was set up to test the difference in performance between two types of resin (Purolite and Lanxess). Each of the columns was filled with 50L of virgin resin material and was subject to pretreated water, the same as the first large column set up. The adsorption data is summarized in FIGURE 24. The two types of material performed similarly throughout the experimental period. At the spike in inlet concentration from 400-800 bed volumes, Purolite resins seem to perform slightly better than the Lanxess resins. Both however retain>90% removal of PFAS after 4,300 bed volumes. The difference in performance is primarily attributed to Lanxess being less efficient in the adsorption of PFOSA, compared to Purolite (data not shown).

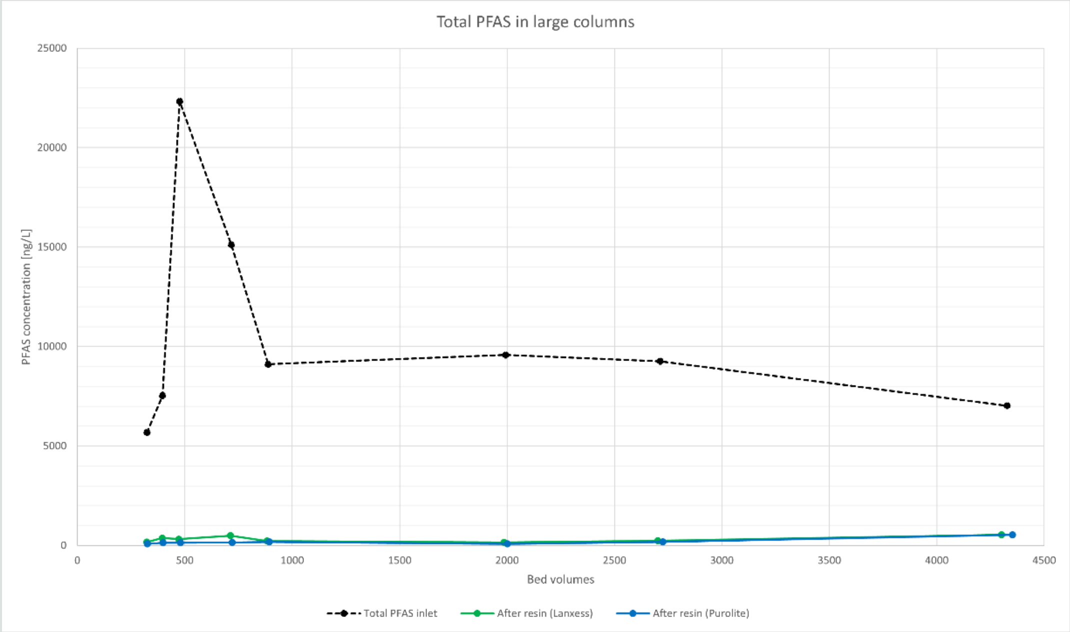


FIGURE 24. Comparison of large-scale columns containing two different resin types (Purolite and Lanxess). The largest single PFAS component in the inlet water is PFOS.

4.3 Effect of pretreatment on PFAS adsorption capacity

As established, the removal of organic material has a positive impact on PFAS adsorption capacity. The following set of experiments were set up to quantify this effect using different combinations of pretreatment, followed by adsorption experiments. These experiments were first set up on a laboratory scale, followed by on-site pilot scale experiments at Audebo landfill (Denmark).

4.3.1 Laboratory evaluation of leachate pretreatment effect on adsorption column life span

The impacts of pH and dosage of Fluorfloc on the removal of PFAS in leachate pretreated with coagulation and flocculation were studied, and the results are shown in FIGURE 25 and FIGURE 26. The applied dosages for poly aluminum chloride and polymer were 0.3 and 0.04 ml/L, respectively. Coagulation and flocculation were carried out using a jar test setup that included six propellers and a speed controller. Immediately after adding poly aluminum chloride and Fluorflok into 1 L of glass beaker with leachate placed underneath the propeller, the speed controller was turned on for 30 seconds of rapid mixing with 1000 rpm. After that, the polymer was added into the beaker and the mixing speed was decreased to 200 rpm followed by 5 minutes of slow mixing. Then the speed controller was switched off and let the leachate settle for 30 minutes before the supernatant samples were taken for the PFAS analysis.

The increase of the PFAS removal was in line with some previous studies, where the increase of sorption with increasing solution pH in the presence of Ca^{2+} or Mg^{2+} in water because the adsorbent surfaces developed more basic sites to bind divalent cations when pH increased, resulting in the enhanced sorption of PFAS through divalent cation bridging effect (Du et al., 2014).

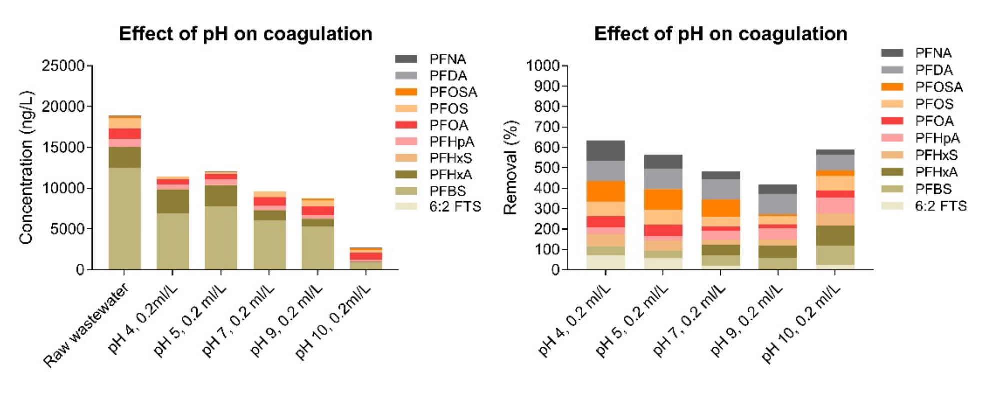


FIGURE 25. The impact of pH on the removal of PFAS in leachate pretreated with coagulation and flocculation. 0.3 ml/L of poly aluminum chloride, 0.04 ml/L of polymer, and 0.2 ml/ of Fluorflok were applied.

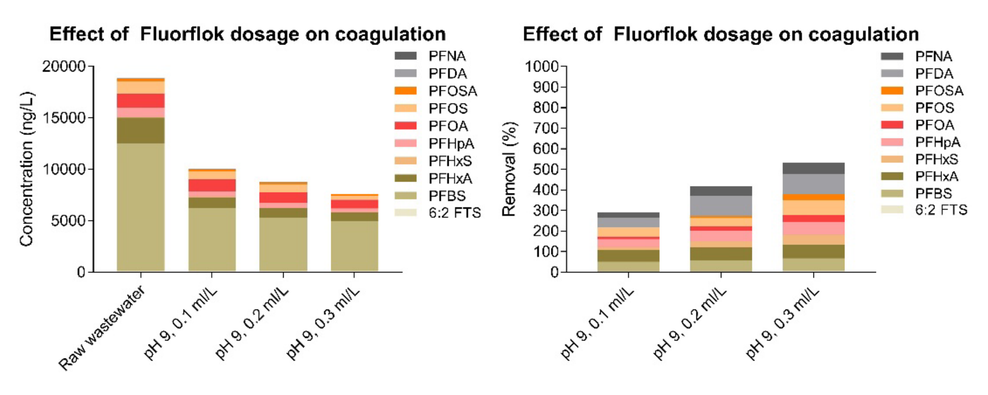


FIGURE 26. The impact of dosage of Fluorflok on the removal of PFAS in leachate pretreated with coagulation and flocculation. 0.3 ml/L of poly aluminium chloride and 0.04 ml/L of polymer were applied. pH was fixed at 9.

The effect of Fluorfloc, a flocculant, specifically designed for PFAS removal, in addition to the PAX coagulation, was tested on Audebo Miljøcenter leachate, and the results are presented in FIGURE 27. This leachate differs from the leachate experiments in FIGURE 25 and FIGURE 26.

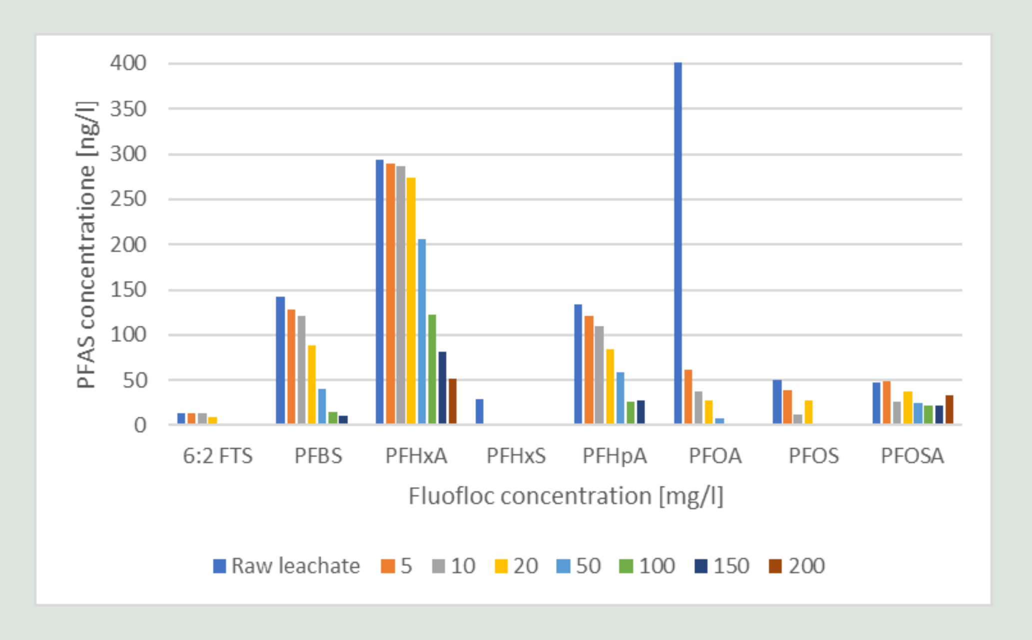


FIGURE 27. PFAS concentration in raw leachate from Audebo Miljøcenter as well as treated with PAX (500 ml/m^3) and varying concentrations of Fluofloc (numbers in the nomenclature represent Fluorfloc concentrations applied in mg/l). The PFOA concentration in raw leachate was 880 ng/l exceeding the presented scale.

The PAX/Fluorfloc experiment was conducted at the original pH value of 8,2. Fluorfloc showed the highest removal efficiency for long-chain carboxylic PFAS and higher concentrations of Fluorfloc were necessary for the removal of short-chain PFAS. PFOA was removed by 93 % and PFHxS to below the detection limit with a Fluorfloc addition of only 5 mg/L, while the other PFAS compounds were only removed between 0 and 22 %. With Fluorfloc addition of 200 mg/l, all PFAS compounds except PFHxA (82 %) and PFOSA (approximately 50 %) were removed to below the detection limit (TABLE 2).

TABLE 2. Removal efficiency (%) with the addition of different concentrations of Fluorfloc flocculant after coagulation with PAX (500 ml/m3). 100* indicates that the PFAS was not detected in the treated leachate above the detection limit, which is displayed as 100% removal.

Fluorfloc concentration [mg/l]	**Removal efficiency (%)**							
	6:2 FTS	**PFBS**	**PFHxA**	**PFHxS**	**PFHpA**	**PFOA**	**PFOS**	**PFOSA**
5	5	11	2	100*	9	93	22	-3
10	2	15	3	100*	18	96	77	45
20	30	38	7	100*	37	97	46	23
50	100*	72	30	100*	56	99	100*	48
100	100*	89	58	100*	80	100*	100*	53
150	100*	93	72	100*	79	100*	100*	54
200	100*	100*	82	100*	100*	100*	100*	31

4.3.2 Effect of pretreatment on adsorption capacity (pilot scale at Audebo Miljøcenter)

To further examine the impact of pretreatment on the lifespan of the adsorption material, a pilot-scale test was established at Audebo Miljøcenter. The leachate utilized for the tests was simultaneously gathered from the buffer tank, which contained a blend of leachate from all deposit cells. Ten 1m^3 containers were filled with leachate, 100L in each at a time, to reduce heterogeneity as much as possible. The organic content of this leachate measured in COD was 360 mg/l. Leachate from each different pretreatment strategy was polished with ion-exchange resins (Purolite PFA694E) and the removal of PFAS was monitored in the outlet water. The following PFAS were analyzed in all cases as sum 14: PFBS, PFPeA, PFHxS, PFHxA, PFHpA, PFOA, PFOS, PFOSA, 6:2 FTS, PFDA, PFNA, PFDoA, PFTrDA and PFTeDA. The reason for these 14 PFAS was that analytical standards were available for these. The different pretreatment strategies employed during this series of experiments are clarified in TABLE 3.

TABLE 3. Summary of the experimental setup at Audebo Miljøcenter. Experiment #4 is without pretreatment to serve as a reference.

Experiment number	Pretreatment	First column	Second column
1	Ozone skimming	Resin	-
2	PAX + filtration	GAC	Resin
3	PAX + filtration	Resin	Resin
4	-	Resin	-

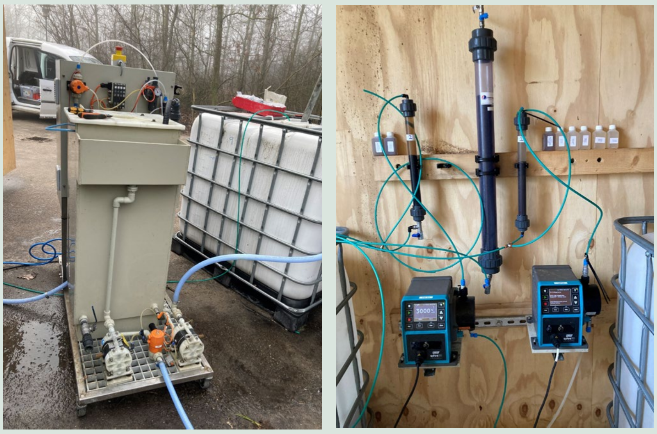


FIGURE 28. Left: Filtration system for treatment after coagulation/flocculation. Right: GAC (the column in the center) and resin columns.

Untreated leachate was led directly onto the resin column (150 ml bed volume, flow: 20 BV/h) and served as a reference (experiment 4). Different pretreatment strategies were evaluated during this pilot scale test and are described in the following.

Ozone skimming

Ozone skimming was performed for three hours using continuous recirculation through a recirculation tank equipped with a venturi. The gas flow from the generator was 6 liters/min and the ozone was generated using a Primozone GM2 generator (100 g O_3/hour). During the test, the leachate changed color visibly (FIGURE 29).

FIGURE 29. Leachate before (right) and after (left) ozonation treatment.

The pretreated leachate was transferred to the resin column (150 ml BV, 20 BV/h) as illustrated in FIGURE 30.

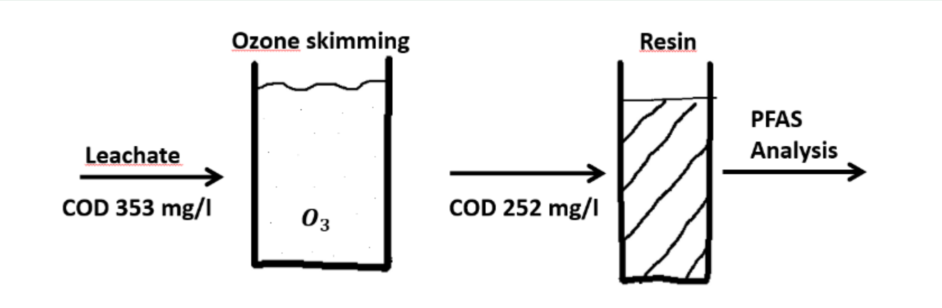


FIGURE 30. Schematic drawing of the ozone skimming pretreatment and resin adsorption step.

Coagulation/filtration followed by GAC and resin columns
Coagulation was performed with PAX (0,5 l/m^3) followed by ceramic membrane filtration (0,1 µm pore size) before the pretreated leachate was pumped to a GAC column (600 ml BV, 5 BV/h). The outlet leachate was collected in a buffer tank, stirred, and afterward transferred to the resin column (150 ml BV, 20 BV/h) as illustrated in FIGURE 31.

FIGURE 31. Schematic drawing of the coagulation/filtration pretreatment and the granulated active carbon adsorption followed by resin adsorption. The COD concentrations in the different steps are indicated.

Coagulation/filtration followed by two consecutive resin columns

Coagulation was performed with PAX (0,5 l/m^3) followed by ceramic membrane filtration (0,1 µm cut off) before the pretreated leachate was transferred to a resin column (150 ml BV, 20 BV/h). The outlet leachate was collected in a buffer tank, stirred, and afterwards transferred to the second resin column (150 ml BV, 20 BV/h) as illustrated in FIGURE 32.

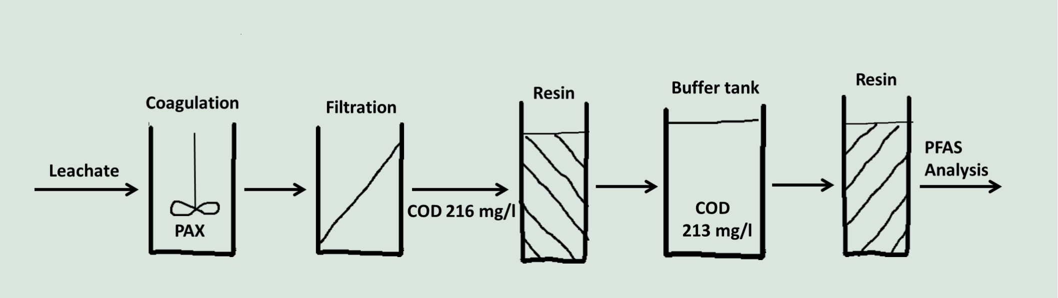


FIGURE 32. Schematic drawing of the coagulation/filtration pretreatment and the adsorption steps with two resin columns. The inlet COD concentrations for both columns are indicated.

FIGURE 33 shows results for total PFAS sum 14 observed in the different treatments.

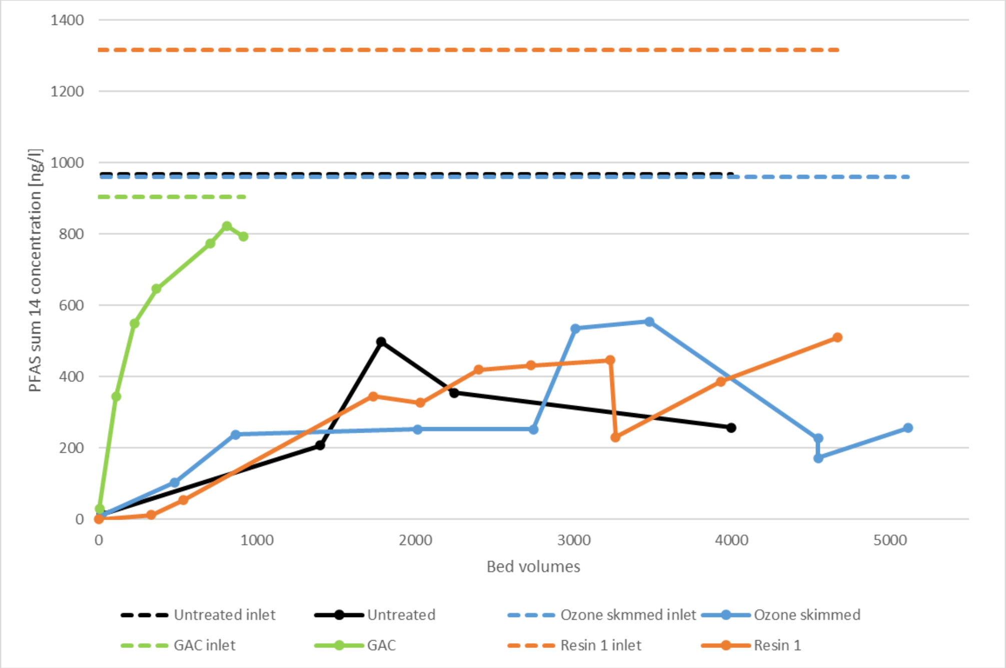


FIGURE 33. Monitored total PFAS sum 14 concentrations in outlet from different adsorption columns after different pretreatments. The dotted lines represent inlet concentrations.

The PFAS inlet concentration in the Resin 1 test was significantly higher than in the GAC, untreated, and ozonated experiments, even if there were made efforts to collect the leachate simultaneously from the buffer tank for all experiments. A rapid change in the concentration of leachate can occur, as leachate from different cells with significantly different PFAS concentrations is pumped into the buffer tank one by one. If there is a change in the pumping process while collecting the leachate from the tank, fluctuations in the collected leachate can occur, as the only collection point available is near the inflow to the leachate tank.

A rapid breakthrough was observed on the GAC column (nearly complete breakthrough within 800 BV), indicating that GAC adsorption is not a preferable method for removing PFAS from leachate (FIGURE 33). This observation is further supported by measurements on another leachate, in which GAC also exhibited rapid breakthrough (FIGURE 20). There could be other reasons, such as the adsorption of other unwanted molecules, that could justify the use of GAC. The breakthrough of both short and longer-chain carboxylic PFAS acids, as well as the short-chain sulfonic PFAS (PFBS) present in the leachate, occurred after a maximum of 100 bed volumes. After 900 bed volumes, a complete breakthrough (100% of the inlet concentration) was observed for almost all PFAS (FIGURE 46). The pretreatment coagulation and filtration resulted in a COD reduction of 15 %. The GAC column reduced the COD by an additional 18 %.

The use of resin adsorption in the Resin 1 experiment extended the breakthrough time significantly (approximately 500 BV in comparison with instant breakthrough with GAC column – no data available for untreated and ozone skimming in this early stage of the test). Breakthrough still occurred quite rapidly despite pretreatment with PAX and filtration, which reduced the organic content from COD 370 mg/l to 216 mg/l (42 %). The concentration of PFAS remained at a maximum of 58% of the inlet concentration (untreated = 51 %, ozone skimmed = 58 %, resin 1= 39 %) during the bed volumes tested, which showed a much higher PFAS removal efficiency of resin than GAC adsorption. Unlike GAC, the resin is capable of adsorbing short-chain sulfonic PFAS, as no breakthrough of PFBS was observed (FIGURE 47).

The pretreatment with coagulation, involving the use of PAX and membrane filtration, did not result in any measurable reduction of PFAS, and the trend of the curve for the resin 1 test, which underwent pretreatment, is identical to that of the untreated leachate. This contradicts the experiences of Vandrensning.com from other sites, where pretreatment significantly prolongs the lifetime of the resins and also the findings of other experiments in this project, see e.g. FIGURE 8 where pretreatment significantly improved the performance of the resins. Looking at the specific PFAS compounds (short carboxylic acids (PFPeA and PFHxA), the breakthrough appears slower in the column with pretreatment and does not reach full breakthrough (FIGURE 44 and FIGURE 47).

It was shown that even untreated leachate on resin was much more effective than pretreated leachate on GAC. In the untreated leachate, a higher degree of breakthrough was observed with decreasing chain length of the PFAS molecules, and no breakthrough was observed for sulfonated PFAS compounds such as PFBS and PFOS (FIGURE 44).

The ozone skimming pretreatment resulted in an organic content (COD) reduction of 29 % but had no effect on PFAS removal. On the resin column, shorter chain carboxylic acids (PFPeA and PFHxA) showed breakthrough after 860 BV, while the longer chain PFAS breakthrough was detectable over 30 ng/l, which is the limit of detection (LOD), at 3000 BV. The general decrease of PFAS after 3500 BV is lacking an explanation (FIGURE 45).

An interruption of flow over the columns (5 days resin 1 – 3200 BV and 8 days ozone skimmed – 4540 BV) led to a temporary decrease in the PFAS concentration in the outlet. Further investigations should be made to investigate, whether this effect can be utilized.

The efficiency of resin adsorption can be observed in FIGURE 34, where the leachate is pretreated either on a GAC or resin column.

FIGURE 34. Monitored total PFAS sum 14 concentrations in outlet from different consecutive adsorption columns. The dotted lines represent inlet concentrations.

The pretreatment on a GAC column removed 31 % of the total PFAS (PFAS sum 14: GAC inlet leachate: 905 ng/l, average in outlet leachate: 626 ng/l) and 21 % of the COD (297 mg/l to 235 mg/l). The volume treated in the GAC column is equivalent to the volume treated in the resin column, as the bed volume for GAC is four times larger than that for resin. Breakthrough of PFPeA and PFHxA occurred after 500 bed volumes (FIGURE 48), as also seen when the leachate was transferred directly to the resin column (FIGURE 47). Hence no significant improvements were achieved by implementing a GAC column before the resin column, probably because the COD removal on the GAC column was not sufficient to significantly influence the result.

Pretreatment on a resin column reduced the PFAS concentration by 75 % in the volume treated (PFAS sum 14: resin inlet leachate: 1315 ng/l, average outlet leachate: 323 ng/l). No PFBS was monitored in the inlet leachate for the second resin column, as it was fully withheld in the first resin column. Breakthrough of PFPeA occurred at 500 BV on both columns, while breakthrough of PFHxA was prolonged to more than 500 BV, and PFHpA breakthrough was prolonged to more than 2750 BV (FIGURE 49). The COD concentrations in the inlet for both resin columns were almost identical (213 and 216 mg/l), and the BV treated before PFAS breakthrough was only prolonged slightly for some PFAS. This emphasizes, that the COD concentration in the leachate is a more crucial parameter for resin capacity than the PFAS concentration itself. Furthermore, it can be concluded, that the removal of PFAS is more selective on resin than on GAC, which also was concluded by Malovanyy et al. (2023).

5. PFAS destruction

SCWO has proven very efficient for the mineralization of PFAS compounds regardless of media type, concentration, and type of PFAS compound.

This section of the report describes the effectiveness and possibilities of using Supercritical Water Oxidation (SCWO) technology provided by Aquarden Technologies (henceforth "Aquarden") for the destruction of concentrated PFAS e.g., from landfill leachate. Aquarden Technologies produces and delivers full-scale SCWO equipment, the SuperOx®, which operates continuously with complete automation, using the working principle of SCWO. SuperOx® can operate at SCWO conditions, i.e., above the critical point of water (374 °C, 221 bar), or at subcritical conditions for high-salinity wastewater treatment (below 374 °C). A series of SCWO tests conducted for this project, using both a laboratory-scaled reactor and a full-scale plant, have proven complete mineralization of PFAS in various solutions/media with PFAS concentrations between 3000 and 86 000 µg/L.

FIGURE 35. Aquarden's SuperOx®, full-scale SCWO system (left) and laboratory-scale system (right).

Oxidation in Supercritical Water

Water reaches supercritical conditions above 374 °C and 221 bar, where the density of water approaches that of a gas, and the liquid-gas phases become indistinguishable. There is no direct phase change to the supercritical fluid at the critical point, as the properties of the supercritical fluid (density etc.) vary continuously with temperature and pressure (Kutz 2007).

Supercritical water possesses properties of both gas and liquid, meaning it has solvating properties closer to that of liquid and mass transfer properties closer to that of gas, and with the intermolecular changes of the water it becomes a great solvent for organic matter as well as gasses. As gases can be homogeneously mixed into the supercritical fluid, introducing oxygen under these conditions will create an aggressive and rapid oxidation of organic compounds, which within seconds decompose to CO2, N2 and H2O. Organically bound halogens, like fluoride, oxidized under these conditions will create mineral acids, while free salt ions become insoluble and precipitate. No ash or sludge phase is generated during the process, as the feed enters as a pumpable liquid or a particulate slurry, and the effluent exits the reactor system as a liquid. In addition to the liquid effluent, is the gaseous effluent consisting mainly of CO2, N2, and excess O2 from the oxidation.

At supercritical conditions, there is a natural limitation as to how much base can be used for neutralizing the acid generated during the oxidation, due to the low solubility of the salts as an effect of a very low dielectric constant and almost non-polar nature of the water at this state. This limitation and acid-base-balance is very important to keep in mind when working with PFAS destruction as it will be a limiting factor. If correct acid management is not applied, there is a risk of creating a highly corrosive environment in the SCWO reactor.

Destruction of PFAS

A major advantage of SCWO, is the capability of handling and completely mineralizing high concentrations of PFAS. When it is possible to treat a concentrated stream, it makes sense from a commercial standpoint to utilize the capacity of the SCWO system during the destruction process.

In leachate, the average PFAS concentration is typically only 1000 – 50 000 ng/l depending on the leachate source, meaning that it is beneficial to concentrate the PFAS in the leachate even further prior to SCWO treatment.

As described previously in this report, there are several commercially available technologies for capturing and concentrating PFAS from e.g., landfill leachate. Common to these technologies are that, aside from Reverse Osmosis (RO) membranes, they do not concentrate the salts present in the leachate and instead almost provide a secondary salt removal while concentrating the PFAS. Removing the salts prior to treating the PFAS from a landfill is very beneficial for the SCWO technology, as excessive amounts of salt precipitated in the reactor can cause operational downtime due to the potential need of salt-flushing.

With most of the PFAS-compounds consisting of >60 % w/w fluorine, knowledge of the PFAS concentration span in the feed for SCWO is important to predict the amount of acid generated during the oxidation. With the goal of maintaining a stable, neutral pH of the effluent water during operation, proper acid management becomes a key element.

Each concentration technology will generate its own unique type of PFAS waste. During this project, the focus has mainly been on adsorbents such as ion exchange resins and activated carbon. Once the PFAS is collected on the adsorbent, the adsorbent can be crushed into a slurry and destroyed together with the adsorbed PFAS in the SCWO system. An alternative method is desorbing the PFAS from the adsorbent through regeneration of the material and treat a regenerant containing PFAS with SCWO while the adsorbent is reused.

The tests on PFAS saturated adsorbents presented later in this chapter focuses solely on the destruction of spent single-used adsorbents as well as the destruction of concentrated PFAS from firefighting foam.

How to ensure complete mineralization of PFAS with SCWO
There are thousands of PFAS compounds and most analysis focuses only on ~20-30 of these. Aside from the usual PFAS suspects, there are also a variety of precursors and once you apply an oxidation technology and start to break down these chains it can become difficult to predict the potential intermediate products that could be formed during the oxidation reactions.

In the liquid effluent, the content of organically bound fluorine is analyzed to show that the carbon-fluorine chains are completely gone, while the free fluoride is analyzed as this is the final product.

Usually, PFAS sum 22 is also added to the analytical package, but this is mainly to keep up with the discharge requirements as it is the two other analyses (AOF and inorganic fluoride) that really enlightens what happens to the PFAS in the SCWO process. In the tests presented later, not all the fluoride was detected in the effluent, due to accumulation of fluoride salts in the sub-critical region of the reactor (below the critical point of water), as higher concentrations of fluoride salts were found when the reactor was flushed at lower temperatures.

The gas from the system is also analyzed for fluoride, and while there have not been any signs of fluorinated byproducts in the gas, these results are not presented in this report as the method is still under development.

5.1 Unit description

A simplified PFD of the SCWO system can be seen in FIGURE 36. The wastewater is pressurized and heated in the reactor, while being mixed with the oxidant. In the reactor, the oxidation occurs, and the treated water exits through a heat exchanger to recover the reaction energy before depressurization and gas/liquid separation.

The reactor system is started up with water and switched to the individual waste type once the operational conditions of pressure/temperature are reached. The operational parameters for each test will be described further in the following sections for the individual tests.

To account for any contamination from previous tests (not related to this report), a background sample is taken for each test, before introducing the contaminated feed to the reactor system. This background concentration represents the amount of PFAS released from pipes, tubes, filters etc. and should be subtracted from the PFAS concentration measured in the continuous flow sample during the actual test.

After introducing the feed, at least one hour passes before sampling is initiated. This delay is to prevent the natural dilution factor in the beginning of the test to influence the analysis and ensure steady state operation with the wastewater prior to sampling.

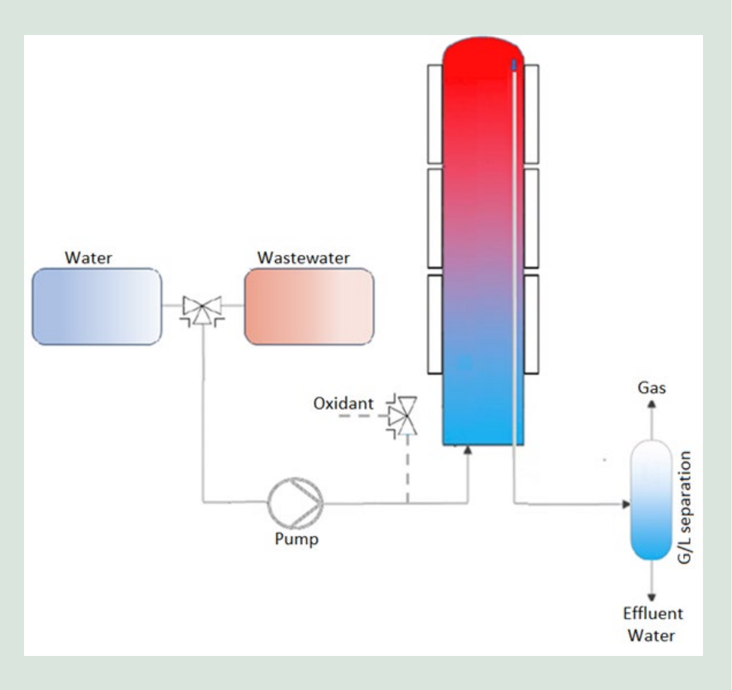


FIGURE 36. Simplified PFD of the SCWO system.

The SCWO system is solely powered by electricity, with no co-fuel added aside from the organic matter in the wastewater. For a highly concentrated organic waste, the heating elements will turn off as the reactor becomes autothermal and the temperature profile stabilizes.

In a continuous flow system, the incoming water will always be at subcritical conditions until it reaches the part of the reactor that allows it to become supercritical, roughly illustrated with the color change in FIGURE 36. This means that there is a section in the lower part of the reactor, where the water is subcritical and has much different properties (e.g. solubility for salts) than in the supercritical region. This knowledge is important to understand why continuous flow samples taken after the liquid/gas separator may contain less salts than expected if only comparing to the inlet concentration. Salts released as part of the oxidation in the subcritical region are likely to accumulate in this section due to the increased solubility compared to the supercritical water and may not be present in the effluent sample as this is taken directly from the supercritical part of the reactor.

For this report, it was decided upon to focus more on the measurable PFAS and AOF than the total mass-balance of the fluorine as this would require a series of tests at subcritical conditions to estimate the degree of accumulation with each different type of wastewater, accounting for different salt compositions and concentrations of PFAS.

5.2 Test 1: Destruction of PFAS contaminated resin in laboratory scale

Two tests were conducted with PFAS contaminated ion exchange resin, one with resin manually spiked with PFAS (test 1A) and one with contaminated resin from a Danish landfill (test 2B). The resin type used for both tests was the purolite PFA694E, anion exchange resin which has a high affinity for PFAS. For both tests, the resin was grinded to a fine slurry with a particle size <50 micron, to accommodate the requirements of the pump in the laboratory scale SCWO system.

5.2.1 Test 1A: Ion exchange resin spiked with PFAS

The slurry contained 1 % w/w of resin with PFAS, resulting in a PFAS concentration of 21 500 µg/L and a COD of ~20 000 mg/L. The exact types of PFAS' adsorbed to the resin were unknown, and not measured for this test as the SCWO process is not selective towards specific PFAS', hence it will not make a difference to the destruction efficiency which types of PFAS' are adsorbed to the resin. Furthermore, the analytical methods for analyzing PFAS adsorbed to resin are yet to be fully developed.

The organic fluorine content was estimated between 12 900 and 15 100 µg/L, based on most PFAS' usually containing 60-70 % fluorine and no other fluorinated compounds were expected to be present in the slurry aside from the 21 000 µg/L of PFAS.

To ensure the released fluoride and sulphur end up in their corresponding salt-forms, the slurry was pre-neutralized with base to a pH of 13 prior to the SCWO treatment. In TABLE 4, the operational conditions for test 1A are found.

TABLE 4. Operational conditions for test 1A.

Maximum reactor temperature	~600 °C
Reactor pressure	~240 bar
Flow of feed (slurry)	1.2 – 1.4 L/h

The effluent from the SCWO process was collected and analyzed for adsorbable organic fluorine (AOF), ionic fluoride, and PFAS sum 22 at Eurofins Miljø A/S (henceforth "Eurofins"). pH and COD were measured in Aquarden's laboratory. Aside from the effluent sampling, a sample was collected during the test-startup (prior to introducing the feed) to measure the background concentration as this reactor system was suspected to contain trace amount of PFAS from other tests. The background sample taken before introducing the feed slurry showed ~300 ng/L of PFAS and ~60 µg/L of AOF.

5.2.1.1 Results and discussion

The liquid effluent had a stable pH of 7 throughout the test, which is indicative of efficient acid management. All analysis of PFAS and AOF showed values below that of the initial background sample, and when comparing effluent analysis to the initial concentration in the feed, the destruction efficiency of PFAS sum 22 was calculated to >99.9996 % for all effluent samples and >99.9 % for AOF (see TABLE 5). In the effluent, AOF and PFAS sum 22 were measured at ~20 µg/L and ~60 ng/L respectively, which could be a result of the background contamination of the system proven by the background sample.

More than 99.97 % of the COD was removed (measured below the detection limit of 5 mg/L), proving a complete destruction of the adsorbent as well.

TABLE 5. Destruction efficiency after SCWO test 1A, of PFAS contaminated ion exchange resin. *Calculated value for AOF.

	Feed	**Sample1 After 1h**	**Sample2 After 2h**	**Sample3 After 3h**
COD	~20 000 mg/L	>99.97 %	>99.97 %	>99.97 %
AOF	~15 100 µg/L*	>99.9 %	>99.9 %	>99.9 %
Sum 22 PFAS	21 500 µg/L	>99.9996 %	>99.9997 %	>99.9998 %

No color, odor or residue were observed in the samples after test 1A. Accumulation of fluoride salts in the lower part of the reactor made it difficult to generate a complete mass-balance for the fluoride throughout the system. Approximately 60 % of the expected free fluoride (estimated based on the calculated value of AOF) was recovered in the liquid effluent (continuous flow sample). Due to the dilution applied during shutdown it was not possible to calculate the amount of fluoride salts accumulated in the reactor and filter, but all of it was easily flushed from the system and did not result in any complications throughout the test.

5.2.2 Test 1B: PFAS contaminated resin from Danish landfill

The slurry for test 1B, contained 0.6 % w/w of PFAS contaminated resin, with an estimated PFAS concentration of 3-5000 µg/L. Based on the PFAS analysis on the leachate from the landfill, the PFAS' adsorbed on the resin were expected to mainly be 6:2 FTS, PFHpA, PFHxA and PFPeA. It should be noted that the estimated concentrations of PFAS have some uncertainties due to assumptions made regarding i) flowrate, ii) stability of the PFAS concentration over time, iii) that all PFAS were captured by the resin and iv) that the PFAS was evenly distributed throughout the resin column.

It is safe to assume that other compounds from the leachate, both organic and inorganic, could have accumulated on the resin during the polishing step as well.

With an estimated concentration of 3-5000 µg/L PFAS in the slurry used for test 1B, the organic fluorine content was estimated to be between 1800 and 3500 µg/L. The slurry was neutralized with base to a pH of 12 prior to the SCWO treatment. Analysis of the feed slurry showed a COD of approximately 12000 mg/L.

In TABLE 6, the operational conditions for test 1B are found.

TABLE 6. Operational conditions for test 1B.

Maximum reactor temperature	~600 °C
Reactor pressure	~240 bar
Flow of feed (slurry)	1.2 – 1.4 L/h

Prior to starting the test on the resin slurry, a background sample was collected to provide information about any trace amounts of PFAS left over from previous tests. The background sample showed 43 ng/L of PFAS and below the detection limit of AOF (DL = 3 ppb).
The effluent was collected and analyzed for PFAS sum 22 and AOF at Eurofins, while pH and COD were measured in Aquarden's laboratory.

5.2.2.1 Results and discussion

Analyses for COD showed a reduction from 12000 mg/L to below the detection limit of 5 mg/L, meaning a destruction efficiency of >99.95 %.

PFAS sum 22 was measured at ~60 ng/L but contained the same 5 compounds as found in the background sample. The dominating presence of the compounds PFOS, PFHxS and PFBS in the analysis does not match with the expected composition of the resin slurry as this landfill in general experience limited amounts of sulphonated PFAS' aside from 6:2 FTS, hence the 60 ng/L PFAS is expected to originate from a background contamination of sulphonated PFAS' from a previous test at the equipment.

AOF was not detected above the detection limit of 3 µg/L, and combined with the PFAS results, this indicated a very high destruction efficiency for this sample of >99.9 % for the AOF and >99.999 % for the PFAS sum 22. The effluent pH was stable at approximately 6 throughout the experiment. Destruction efficiencies for test 1B can be found in TABLE 7.

TABLE 7. Destruction efficiencies after SCWO test 1B, of PFAS contaminated ion exchange resin.

	Feed	Effluent sample After ~1h
COD	12 000 mg/L	>99.95 %
AOF	1800 – 3500 µg/L*	>99.9 %
Sum 22 PFAS	3000 – 5000 µg/L*	>99.999 %

*Calculated value for AOF and PFAS sum 22.

No color, odor or residue were observed in the samples after test 1B. Upon dismantling the system, accumulated iron was found in the system, originating from the leachate, which could easily be flushed out and did not result in any complications during the test.

5.3 Destruction of PFAS contaminated activated carbon in laboratory scale

Activated carbon is often used alongside ion exchange resin for PFAS capture and it was therefore an important part of the test campaign to include the destruction of activated carbon. The powdered activated carbon (PAC) used for test 2 had a particle size <50 micron and was spiked to a concentration of 10 500 µg/L PFAS. The slurry contained 1 % w/w of PAC and had a COD of ~10 500 mg/L.

It is possible to regenerate the PAC and treat the regenerant using SCWO, however this was not investigated during this test campaign as it has previously been done in another project at Aquarden.

The organic fluorine content was estimated between 6300 and 7400 µg/L and no other fluorinated compounds were expected to be present in the slurry. The PAC slurry was neutralized to a pH of 12 prior to the SCWO treatment which resulted in the PAC particles unexpectedly coagulating and creating larger flocs. These larger flocs caused a decrease in the flow compared to test 1A and 1B.

In TABLE 8 the operational conditions for test 2 are found.

TABLE 8. Operational conditions for test 2, using the Aquarden laboratory reactor.

Maximum reactor temperature	~600 °C
Reactor pressure	~240 bar
Flow of feed (slurry)	0.6 – 0.7 L/h

The coagulation of the PAC particles would have no effect in the full-scale SuperOx® plant, as this can handle much larger particles and higher concentrations thereof. It is simply a matter of the pump of the lab-scale system being more sensitive to larger particles.

The background sample taken prior to the feed being introduced, analyzed by Eurofins, showed ~120 ng/L of PFAS sum 22, and ~44 µg/L of AOF.

5.3.1 Results and discussion

The AOF and PFAS sum 22 analyzed in the effluent were measured below that of the initial background sample and showed a destruction efficiency of PFAS sum 22 of >99.9994 % for all effluent samples while being >99 % for AOF (TABLE 9). All samples had a COD below detection limit of 5 ppm, which provides a destruction of >99.95 %.

TABLE 9. Destruction efficiency after SCWO of PFAS contaminated PAC. *Calculated value for AOF.

	Feed	Sample1 After 1h	Sample2 After 2h	Sample3 After 3h
COD	~20 000 mg/L	>99.95 %	>99.95 %	>99.95 %
AOF	~6300– 7400 µg/L*	>99.1 %	>99.1 %	>99.2 %
Sum 22 PFAS	10 500 µg/L	>99.9994 %	>99.9994 %	>99.9994 %

No color, odor or residue were observed in the effluent samples from test 2. A small amount of inorganic powder from the ~1 % of inorganics in the PAC, was found as residue in the reactor system upon dismantling, however this could easily be flushed out. Around 4000 µg/L of free fluoride was found in the system, which accounts for ~60 % of the expected fluoride. The remaining ~40 % of fluoride was likely accumulated in the reactor as observed during test 1A.

5.4 Test 3: Destruction of PFAS containing firefighting foam

For this 3rd test, Aquarden wanted to test the destruction efficiency of aqueous film forming foam (AFFF) in both the laboratory reactor used for test 1 and 2 as well as with Aquarden's full-scale SuperOx® SCWO plant. This AFFF foam contain around 4000 mg/L of PFAS (mainly PFOS) and is a concentrated foaming agent used for firefighting until it was banned due to its high PFAS content. Aside from the PFAS content, this variant of AFFF also contain ethylene glycol, diethylene glycol butyl ether, alkyl sulphate salts and various thickeners according to the material safety datasheet.

5.4.1 Test 3A: Destruction of AFFF in laboratory scale

The firefighting foam was for test 3A diluted to a COD of ~5500 mg/L and a PFAS concentration measured at 86 000 µg/L, consisting of ~85 000 µg/L PFOS. The operational conditions of the system followed those of test 1A and B, with a maximum temperature ~600 °C and pressure of ~240 bar, as well as a flowrate of approximately 1.2 L/h.

To avoid acid formation, pH of the solution was adjusted to approximately 12 with base prior to the experiment.

5.4.1.1 Results and discussion

AOF was not measured for this specific test, but PFAS sum 22 was reduced by 99.999 %. The trace amounts of PFAS detected in the effluent are expected to be caused by contamination from previous experiments. No background sample was taken for this test as it was not originally planned to be presented as part of the PFASinator test campaign and was conducted with a different scope than to show the complete mineralization of PFAS.

The pH of the effluent was stable at 6 throughout the experiment and the COD was reduced below the detection limit of 15 mg/L.

5.4.2 Test 3B: Destruction of AFFF in full-scale

The firefighting foam was diluted to a COD of ~500 mg/L and estimated PFAS concentration of ~5460 mg/L. In TABLE 10, an overview of the PFAS content in the AFFF can be found.

TABLE 10. Overview of the PFAS mixture used for test 3B, after dilution. This sample was analyzed by ALS global using method 42:2011-03. Some compounds are marked as BDL = below detection limit. Detection limit of PFNA, PFBS, PFDA and 6:2 FTS are 1000 ng/L, while the rest are 10000 ng/L.

Carboxylic acids	PFBA	4700 µg/L	**Sulphonic acids**	**PFBS**	**BDL**
	PFPeA	2700 µg/L		PFHxS	3400 µg/L
	PFHxA	8500 µg/L		PFHpS	14000 µg/L
	PFHpA	6900 µg/L		PFOS	5 400 000 µg/L
	PFOA	12000 µg/L		PFDS	**BDL**
	PFNA	**BDL**	**Fluorotelomers, precursors etc.**	6:2 FTS	**BDL**
	PFDA	**BDL**		8:2 FTS	**BDL**
	PFUnDa	**BDL**		PFOSA	6200 µg/L
	PFDoDa	**BDL**		NEtFOSAA	**BDL**
	PFTrDa	**BDL**		NMeFOSAA	**BDL**
	PFTeDa	**BDL**			

For this test, the temperature of the reactor was set >600 °C with a pressure of ~240 bar. Aquarden's fullscale SuperOx® plant can typically handle continuous treatment flowrates at 180 L/h, but flowrate for this test was set conservatively at 50 L/h to ensure adequate oxidation temperatures due to the low calorific value of the feed. A total of 300 L of waste was treated during this test. The solution was pre-neutralized to a pH between 12 and 13, and the pH was monitored throughout the test.

As for test 1 and 2, a background sample was collected before introducing the AFFF solution to the reactor system. This sample showed no detectable PFAS from the sum 22 list in TABLE 8-7.

5.4.2.1 Results and discussion

The effluent sample collected after >1 h of stable operation, had no detectable PFAS or COD. The PFAS detection limit was 1-10 ng/L depending on the specific PFAS compound while the detection limit for COD was 5 mg/L. This gives a destruction efficiency of the PFAS sum 22 >99.9998 %. AOF was not measured for this specific test, but the test was later repeated with no detectable AOF in the effluent sample.

5.5 Evaluation of SCWO for destruction of PFAS

SCWO has proven very efficient for mineralization of PFAS compounds regardless of solution/media type, concentration, and type of PFAS compound. Aside from the test documented in this report, Aquarden has also tested concentrates from foam fractionation and membranes, raw untreated leachate, concentrated firefighting foam solutions, and wash solutions from GAC regeneration etc., all with similar results and destruction efficiencies above 99.99 %.

It should be noted that >99.9999 % destruction of a highly concentrated amount of PFAS does not necessarily bring the effluent PFAS concentration to an absolute zero. It can be an extra precaution in some cases to apply a simple polishing step to the treated water after the reactor to ensure that no trace amounts of PFAS escape. Any PFAS captured from polishing - whether by resins, carbon or through other treatment steps – can simply be fed back into the SCWO process and completely mineralized.

Gas analysis indicates that the off-gas does not contain any fluorinated compounds, meaning all the PFAS are mineralized to fluoride salts and that no problematic byproducts are generated during the process. The off-gas measurements were not included in the work for this report but it has since the completion of these experiments been documented in various customer projects by Aquarden, that no fluorinated compounds are found in the off-gas from SCWO.

Aquarden is continuously working on identifying and applying the best available analytical methods to further document the complete mineralization of organics and difficult-to-treat contaminants in wastewaters.

6. Large-scale PFAS removal

Large-scale PFAS treatment at landfills has already been implemented at several Scandinavian landfills. The treatment is affordable and can be installed in containers or an isolated tent.

When the project was initiated, there were no full-scale PFAS treatments in place at Danish landfills. However, the project has been overtaken by reality, as several Danish, Swedish, and Norwegian landfills have now implemented full-scale PFAS treatment in their leachate. The specific implementations largely depend on the discharge limits for each landfill, as well as the composition of the leachate.

Below is a brief description of three different landfills where full-scale implementation has been carried out. The cost of PFAS destruction is not included in the calculations.

Ragn-Sells, Norrköping
Basic data:

- PFAS-concentration: 2500 ng/l
- Leachate volume: 12 m^3/h
- Discharge limit: 60 ng/l for PFOS, but also requirements for metals, ammonia, COD, and phosphorous

The landfill already has a treatment system in place, including aerated ponds, bioreactors, and a sedimentation pond. Flocculation was subsequently introduced as the final step, using aluminum chloride, Fluorfloc, and a long-chain polymer. The system has been in operation for 6 months.

The system is installed in an isolated tent to facilitate the smoother handling of chemicals, sludge, etc.

CAPEX: Complete system including dewatering system: 1.650.000 DKK
OPEX: 36 kr./m^3, primarily chemical cost. Energy consumption: 1 kW/m^3.

FIGURE 37. Ragn-Sells, Norrköping, Sweden.

Deponi Syd, Esbjerg, Denmark

Basic data:

- PFAS concentration: up to 95.000 ng/l, dominated by 6:2 FTS but also a large amount of short-chain PFAS
- Leachate volume: 1 m^3/h
- Discharge limit: 100 ng/l for ∑24 PFAS and 2 ng/l ∑4 PFAS

The system is installed in two isolated containers and is rented out to the landfill. Overall it is possible to maintain ∑4 PFAS below 2 ng/l, but it is very difficult to maintain ∑24 PFAS below 100 ng/l due to the large amount of short-chain PFAS in the leachate.

Rental: 45.000 dkk/month

OPEX: 27 kr/m^3, primarily chemical cost, GAC, and Resin, this does not include incineration of sludge which has a very significant input on the price. This system is without sludge dewatering, this will decrease sludge amounts by a factor of 10-14 and thereby reduce sludge incineration costs. Energy consumption 1,8 kW/m^3.

FIGURE 38. Deponi Syd, Esbjerg, Denmark.

Hammerö Sweden
Basic data:

- PFAS concentration: up to 1.600 ng/l
- Leachate volume: 2,5 m^3/h
- Discharge limit: 100 ng/l for PFOS

The system is installed in one isolated container. It is possible to maintain the PFOS content below 60 ng/l for the entire period.

CAPEX: 1.500.000 DKK/month including dewatering of sludge
OPEX: 34 kr./m^3, primarily chemical cost. Energy consumption 1,4 kW/m^3.

7. Heavy metal removal in addition to PFAS removal

When implementing PFAS removal at landfills, addressing the removal of heavy metals at the same time is feasible. It was possible to achieve removal efficiencies up to 84% in a single test, depending on the specific heavy metal.

Leachate contains many other problematic compounds besides PFAS, and heavy metals will impact the receiving activated sludge treatment plant. When applying pretreatment for PFAS removal, addressing the issue of heavy metals simultaneously is relatively straightforward. Consequently, additional experiments were undertaken with the specific objective of removing heavy metals. Heavy metals can be precipitated either by increasing pH to create metal oxides or a sulfite product can be added to use this for precipitation. In the present experiments, the latter was used by adding a commercial sulfide product (Metalsorb). The concentration of dissolved metal can be seen in FIGURE 39. It can be seen that e.g. the solubility of CdS is orders of magnitude lower than $Cd(OH)_2$.

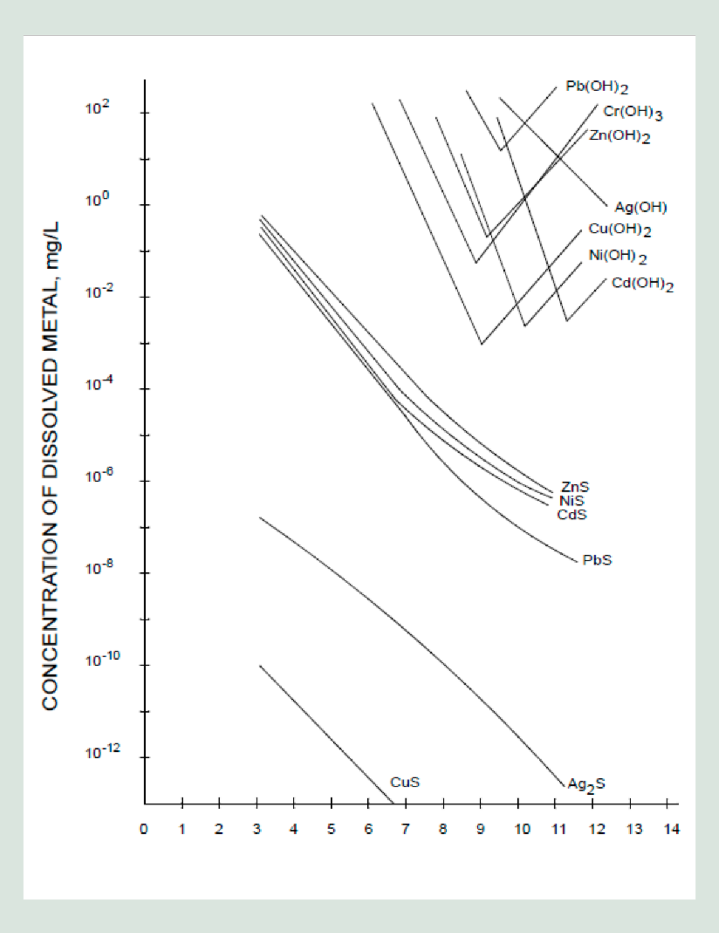


FIGURE 39. Dissolved metal in water at different pH values (x-axis).

Metalsorb is added after the coagulant and prior to the polymer, we have prepared a spreadsheet to calculate the needed concentration of Metalsorb based on the concentration and Mw of the metals (TABLE 11).

TABLE 11. Spreadsheet to calculate the needed concentration of Metalsorb.

Heavy Metals	Mw	Concentration ppm	Metalsorb PCZ ppm
Ag	107,9	30	195,8
Cd	112,4	20	250,6
Cu	63,55	23	509,7
Hg	200,6	23	161,5
Mn	54,9	23	590,1
Ni	58,69	23	552,0
Pb	207,2	23	156,3
Sn	118,7	23	272,9
Zn	65,39	23	495,4
			=
		sum	3184,3

Effects on heavy metal concentrations were measured on leachate from Audebo Miljøcenter, and results are shown in FIGURE 40.

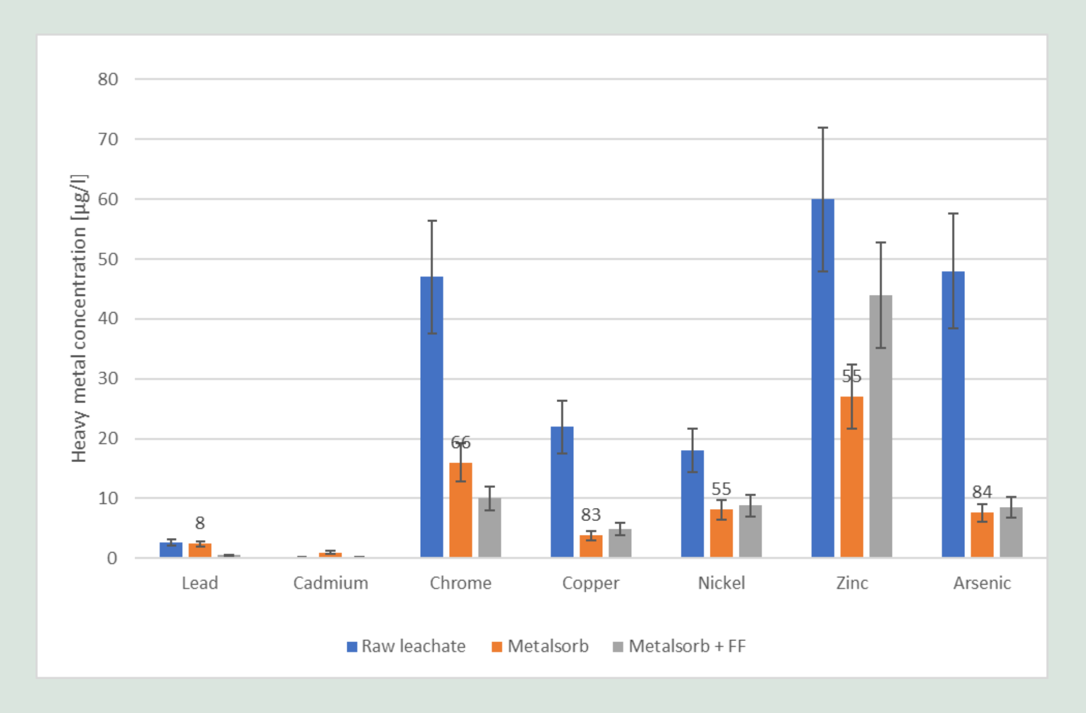


FIGURE 40. The relative analysis is represented by the error bars. Mercury was also the subject of analysis but was not detected. The number displayed above the Metalsorb columns indicates the percentage of heavy metal removal.

For the analyzed heavy metals, the removal percentages ranged from 55 to 84 %, except for lead, which exhibited an 8 % removal rate.

The specially designed PFAS-flocculant Fluorfloc (FF) showed no perceptible impact on heavy metal removal. On the other hand, Metalsorb did not affect the PFAS removal, which is shown in FIGURE 41. To remove both PFAS and heavy metals from the wastewater, Metalsorb and Fluorfloc should be used in combination.

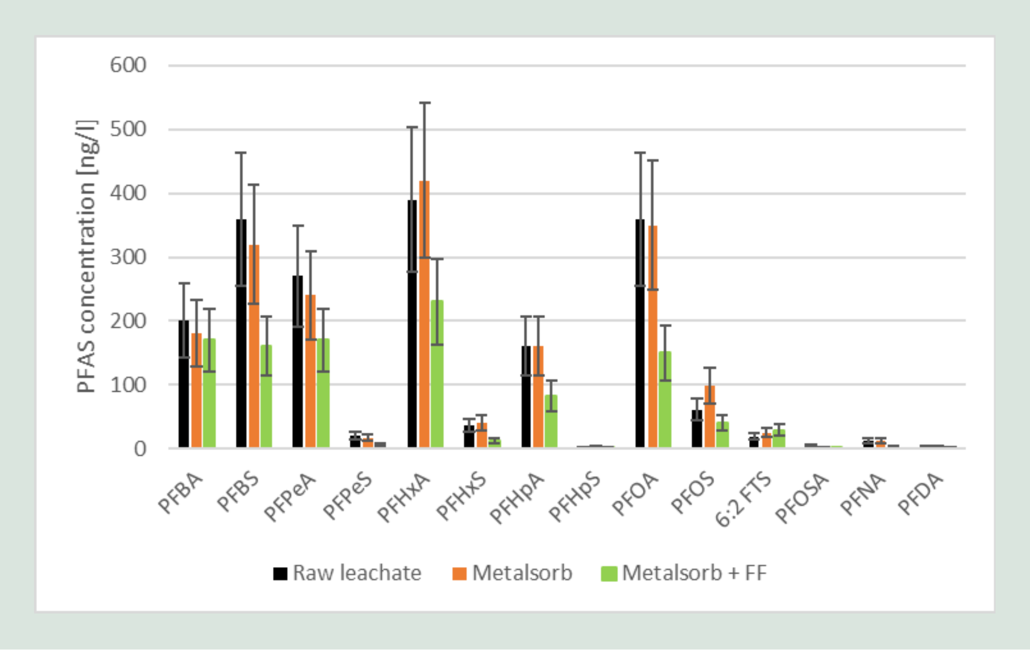
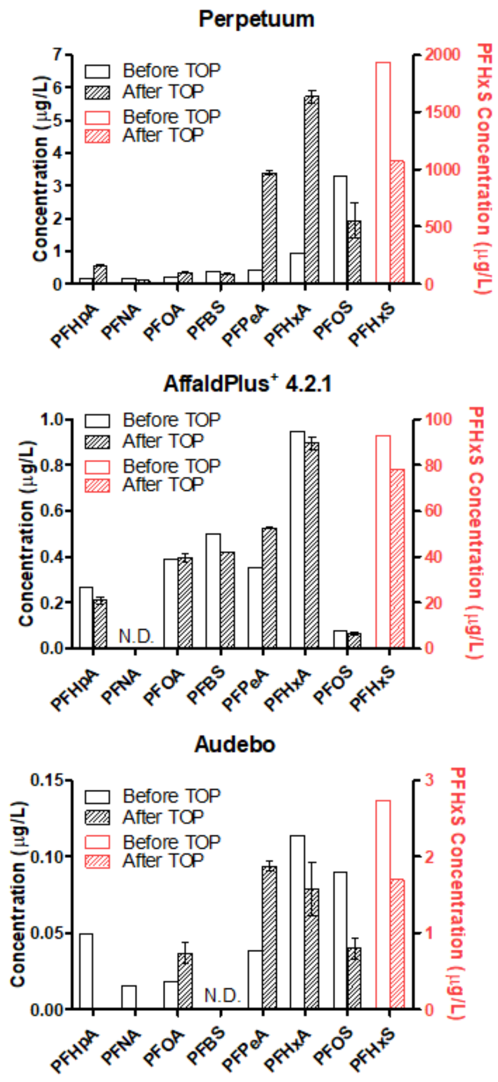


FIGURE 41. PFAS removal by Metalsorb and Fluorfloc dosage. The error bars indicate the relative analysis uncertainty (29 %).

8. Total oxidizable precursor (TOP) assay

Total oxidizable precursor (TOP) assay is a standardized pre-treatment to quantify the potential perfluoroalkyl acid precursors in samples by converting them into known perfluorinated carboxylates through reaction with hydroxyl/sulfate radicals, produced by potassium persulfate under alkaline and heating conditions.

TOP assay was introduced to leachate samples from three PFAS-contaminated locations and the results are shown in FIGURE 42. The concentrations of the studied PFAS in these samples varied before and after treatment with TOP assay, especially the concentration of PFHxS as the dominant compound among all studied PFAS decreased the most, however, the concentrations of PFPeA increased the most except the sample from Perpetuum where the concentration of PFHxA increased the most. The concentration of PFOA slightly increased as well, which also highlighted the importance of the application of TOP assay which could be integrated with the quantitation method of LC-MSMS, to avoid missing a large fraction of the total PFAS concentration in environmental samples.


Perpetuum

AffaldPlus$^+$ 4.2.1

Audebo

FIGURE 42. The changes in the concentration of PFAS of three leachate samples treated before and after TOP assay. N.D.: not detected. Error bars represent standard deviation from duplicate sample analysis.

9. References

Du, Z., Deng, S., Bei, Y., Huang, Q., Wang, B., Huang, J., Yu, G., 2014. Adsorption behavior and mechanism of perfluorinated compounds on various adsorbents-A review. J. Hazard. Mater. 274, 443–454. Link

EFSA 2020, European Food Safety Authority, PFAS in food: EFSA assesses risks and sets tolerable intake, accessed 9 November 2023, Link

Kögel, T., Frantzen, S., Bakkejord, J.A., Kjellevold, M. and Måge, A. 2021. Basisundersøkelse av fremmedstoffer i hyse – tungmetaller, sporelementer og organiske miljøgifter i hyse (Melanogrammus aeglefinus) fra Skagerrak, Nordsjøen, Norskehavet og Barentshavet. ISSN: 1893-4536.

Krause, M.J., Thoma, E., Sahle-Damesessie, E., Crone, B., Whitehill, A., Shields, E. and Gullett, B. 2021. Supercritical Water Oxidation as an Innovative Technology for PFAS Destruction. J Environ Eng (New York). 2021 Nov 23;148(2):1-8. Link

Kurniawan, T.A., Lo, W.H., Chan, G.Y.S., 2006. Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate. J. Hazard. Mater. 129, 80–100. Link

Kutz, M. 2007, page 387-390. Environmentally conscious materials and chemicals processing. John Wiley & Sons.

Malovanyy, A., Hedman, F., Bergh, L., Liljeros, E., Lund, T., Suokko, J. and Hinrichsen, H. 2023. Comparative study of per- and polyfluoroalkyl substances (PFAS) removal from landfill leachate. J Hazard Mater. 2023 Oct 15;460:132505. Link

Meegoda, J.N., Bezerra de Souza, B., Casarini, M.M. and Kewalramani, J.A. 2022. A Review of PFAS Destruction Technologies. Int. J. Environ. Res. Public Health 2022, 19, 16397. Link

Muir, D., Bossi, R., Carlsson, P., Evans, M., De Silva, A., Halsall, C., Rauert, C., Herzke, D., Hung, H., Letcher, R., Rigét, F. and Roos, A., 2019. Levels and trends of poly- and perfluoroalkyl substances in the Arctic environment – An update. Emerging Contaminants 2019, 5, 240-271 Link

National Center for Biotechnology Information, 2023a. Compound summary: Perfluorooctanoic acid. Link

National Center for Biotechnology Information, 2023b. Perfluorooctanoic acid (Annotation): Human Toxicity Excerpts (Complete). Link

Nicolajsen, E.S. and Tsitonaki, K., 2016. Kortlægning af brancher der anvender PFAS. Miljøstyrelsen. ISBN: 978-87-93529-43-4.

OECD 2023, OECD website: Portal on Per and Poly Flourinated Chemicals, accessed 9 November 2023, Link

Salvatore, D., Mok, K., Garrett, K.K., Poudrier, G., Brown, P., Birnbaum, L.S., Goldenman, G., Miller, M.F., Patton, S., Poehlein, M., Varshavsky, J. and Cordner, A. 2022. Presumptive Contamination: A New Approach to PFAS Contamination Based on Likely Sources. Environmental Science & Technology Letters 9 (11), 983-990, Link

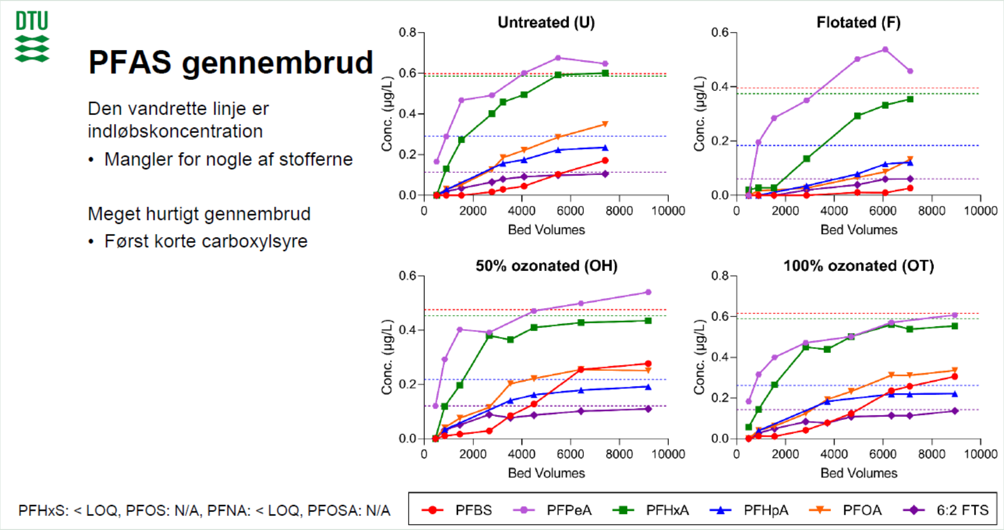
Scheer, 2020. SCHEER (Scientific Committee on Health, Environmental and Emerging Risks), Final Opinion on Draft Environmental Quality Standards for Priority Substances under the Water Framework Directive - PFAS, 18 August 2022. Link

Sonne, C., Desforges, J., Gustavson, K., Bossi, R., Bonefeld-Jørgensen, E.C., Long, M., Rigét, F.F. and Dietz, R. 2023. Assessment of exposure to perfluorinated industrial substances and risk of immune suppression in Greenland and its global context: a mixed-methods study. The Lancet Planetary Health, Volume 7, Issue 7, Pages e570-e579, ISSN 2542-5196, Link

Sundhedsstyrelsen 2023. Helbredseffekter af PFOA, PFNA, PFOS og PFHxS. ISBN 978-87-7014-417-9.

Wang, Y., Ji, Y., Tishchenko, V. and Huang, Q. 2023. Removing per- and polyfluoroalkyl substances (PFAS) in water by foam fractionation, Chemosphere, Volume 311, Part 2, 137004, ISSN 0045-6535, Link

10. Appendix



PFAS gennembrud

Den vandrette linje er indløbskoncentration

- Mangler for nogle af stofferne

Meget hurtigt gennembrud

- Først korte carboxylsyre

PFHxS: < LOQ, PFOS: N/A, PFNA: < LOQ, PFOSA: N/A

FIGURE 43. COD concentrations of inlet water: Untreated = 670 mg/l, Flotated = 274 mg/l, 50 % ozonated = 495 mg/l, 100 % ozonated = 545 mg/l.

Effect of pretreatment on adsorption capacity (pilot scale at Audebo Miljøcenter)

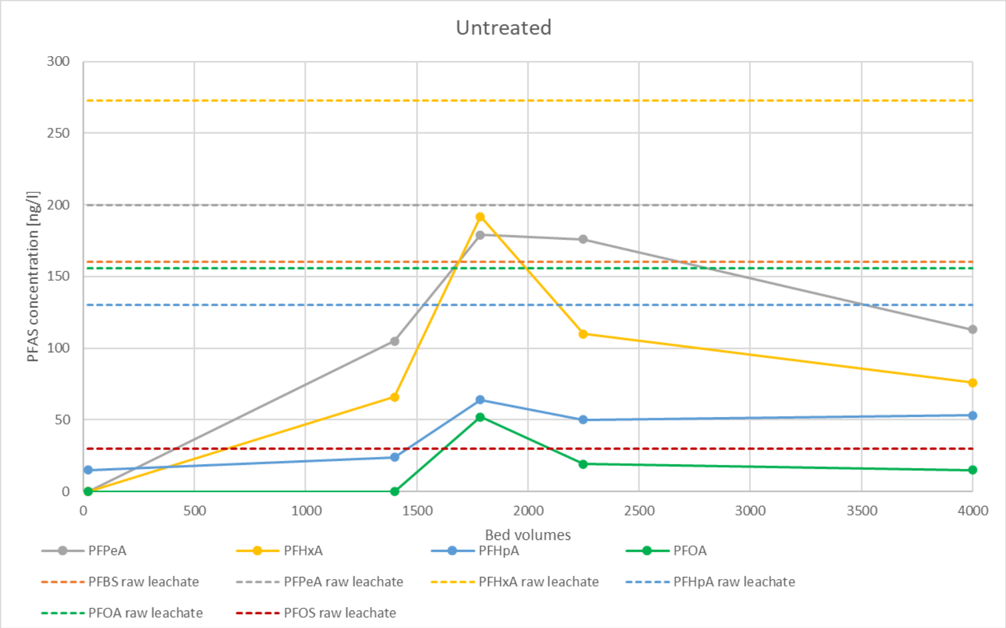


FIGURE 44. Monitored PFAS concentration in outlet from resin treatment of untreated leachate during the time course of up to 4000 bed volumes (BV). The dotted lines represent inlet concentrations.

FIGURE 45. Monitored PFAS-concentration in outlet from resin treatment of ozone skimmed leachate during the time course of up to 5000 bed volumes (BV). The dotted lines represent inlet concentrations. LOD = 30 ng/l.

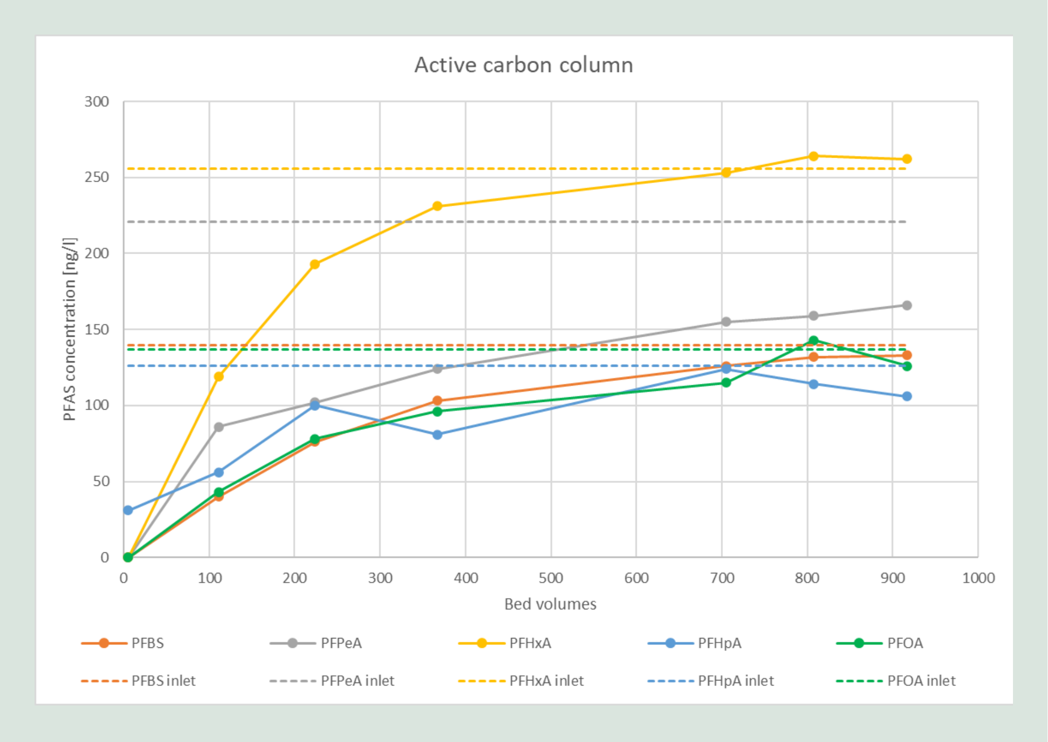


FIGURE 46. Monitored PFAS-concentration in outlet from pretreated (PAX/filtration) leachate on GAC column during the time course of up to 900 bed volumes (BV). The dotted lines represent inlet concentrations. LOD = 30 ng/l.

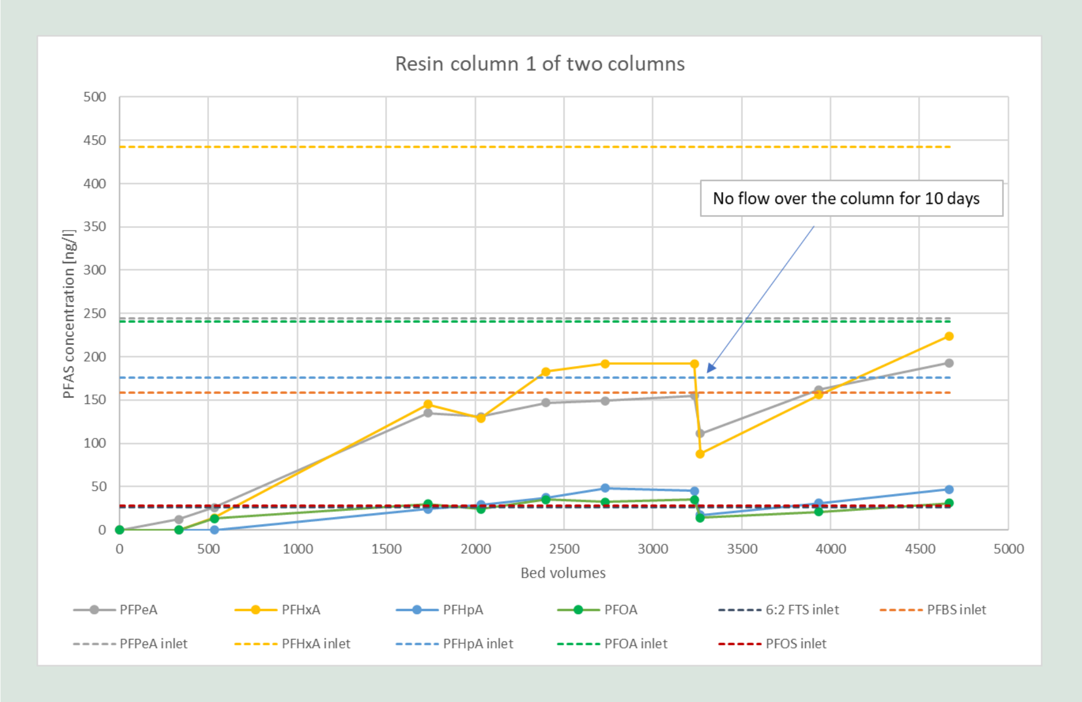


FIGURE 47. Monitored PFAS-concentration in outlet from pretreated (PAX/filtration) leachate on resin column during 4700 bed volumes. The dotted lines represent inlet concentrations. LOD = 30 ng/l.

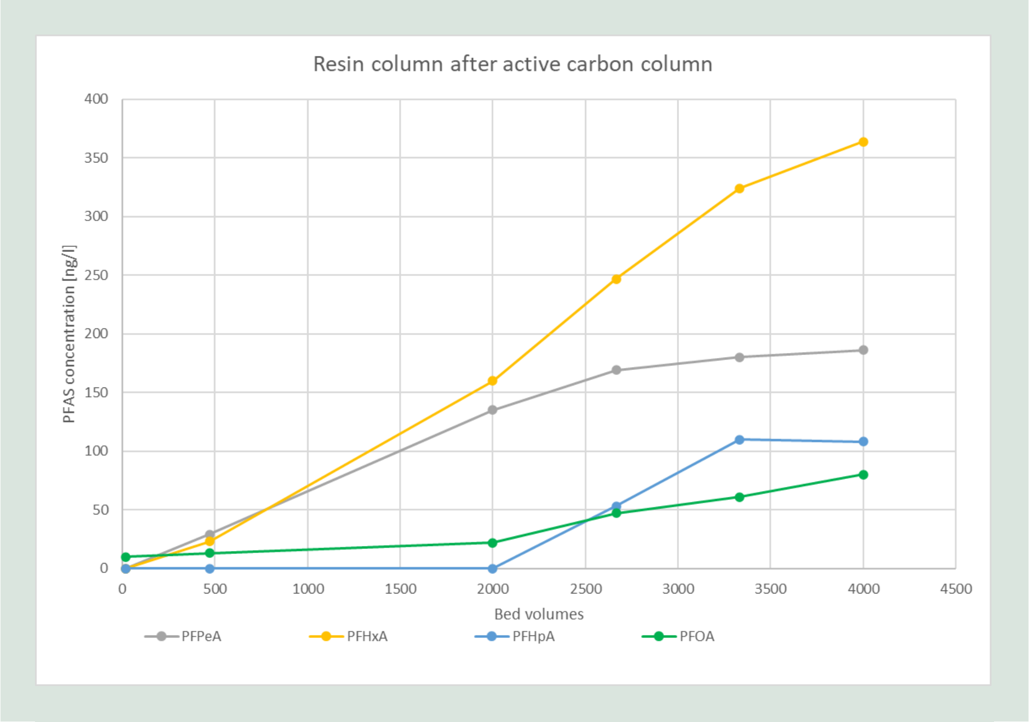


FIGURE 48. Monitored PFAS-concentration in outlet from pretreated (PAX/filtration/GAC adsorption) leachate on a resin column during the time course of up to 4000 bed volumes (BV). The dotted lines represent inlet concentrations. LOD = 30 ng/l.

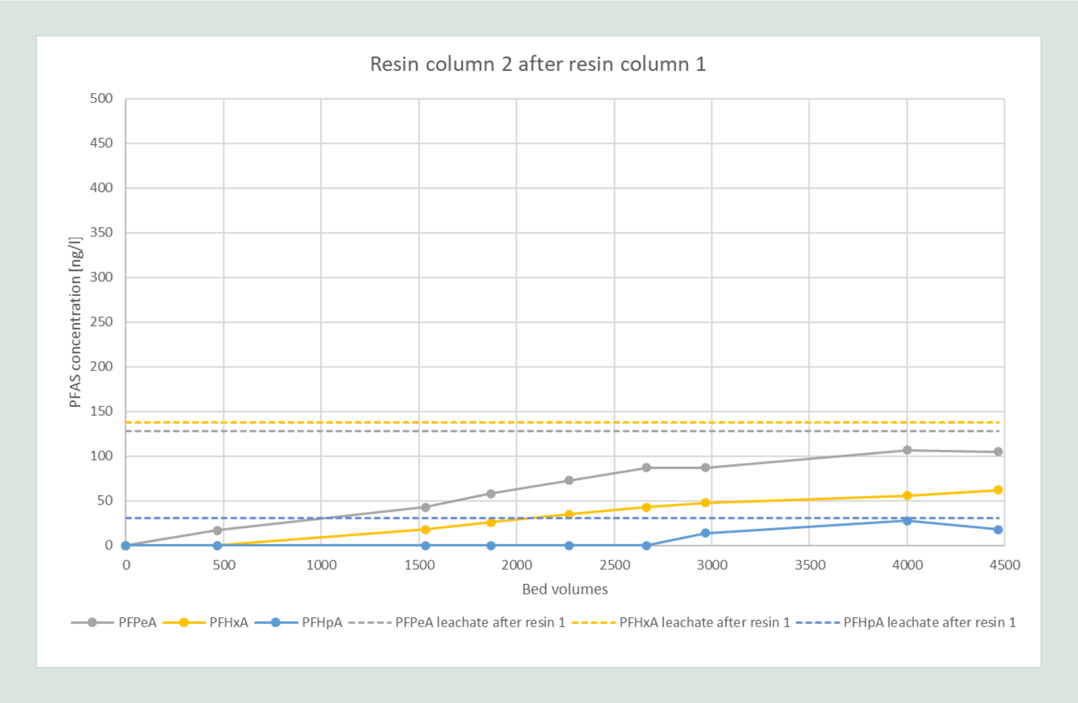


FIGURE 49. Monitored PFAS-concentration in outlet from pretreated (PAX/filtration/resin adsorption) leachate on a second resin column during the time course of up to 4500 bed volumes (BV). The dotted lines represent inlet concentrations. LOD = 30 ng/l.

Appendix 1.1 Resin column graphs

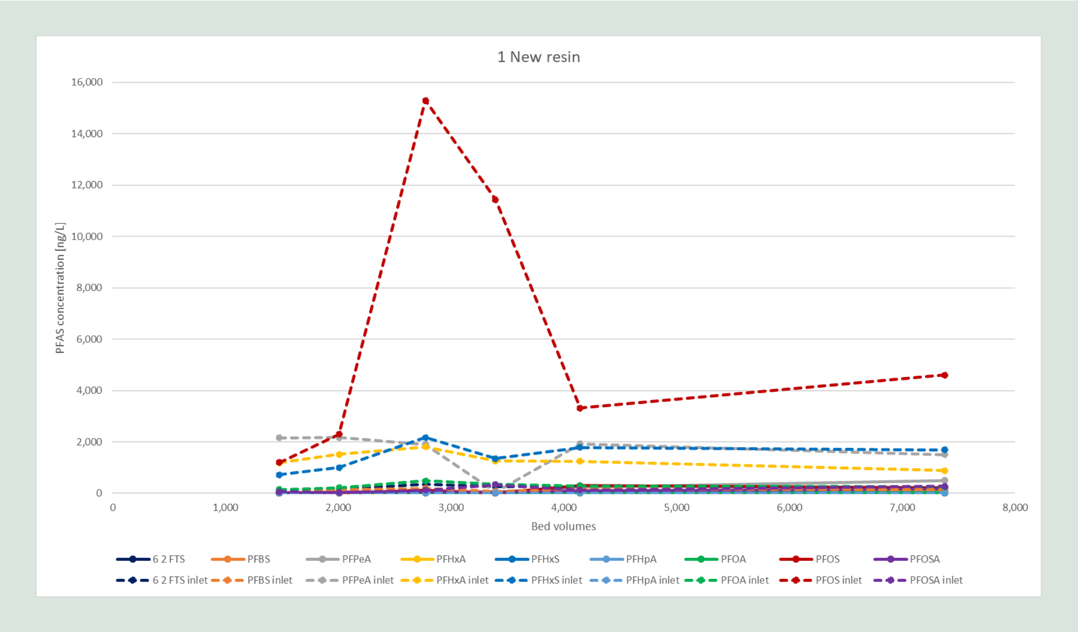


FIGURE 50. PFAS inlet and outlet concentrations of a column containing new resin material. The concentration is plotted as a function of bed volumes through the column.

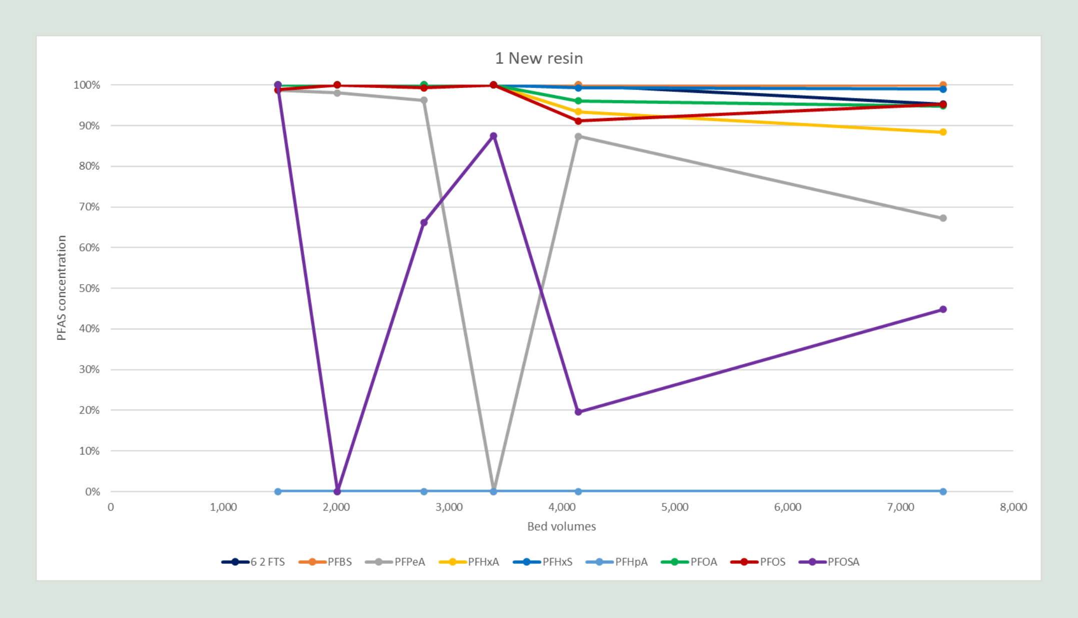


FIGURE 51. PFAS removal percentage as a function of bed volumes in a column containing new resin material.

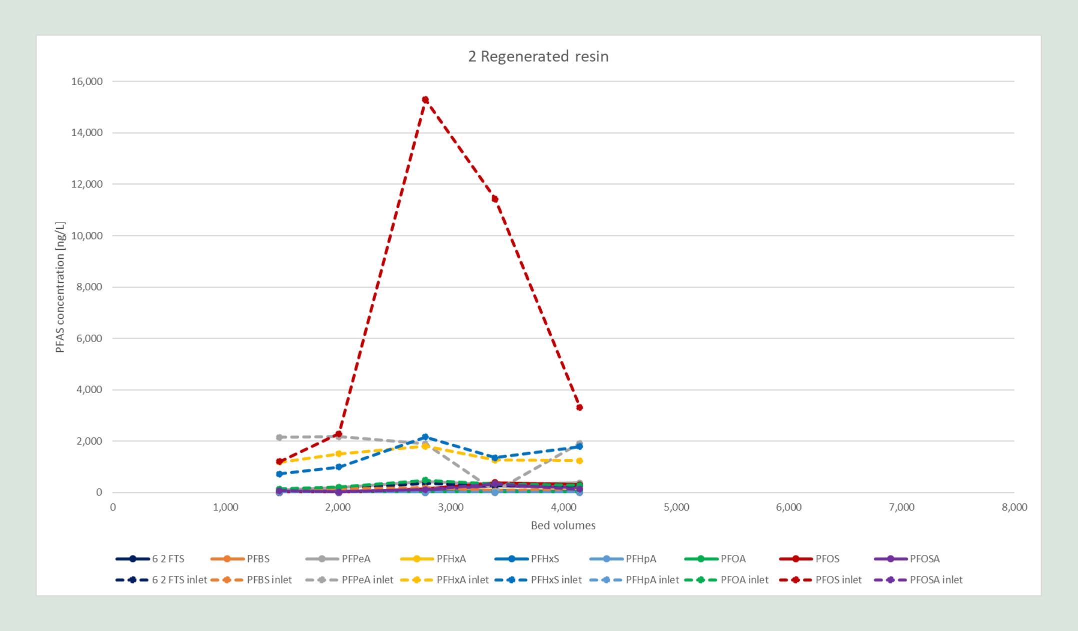


FIGURE 52. PFAS inlet and outlet concentrations of a column containing regenerated resin material. The concentration is plotted as a function of bed volumes through the column.

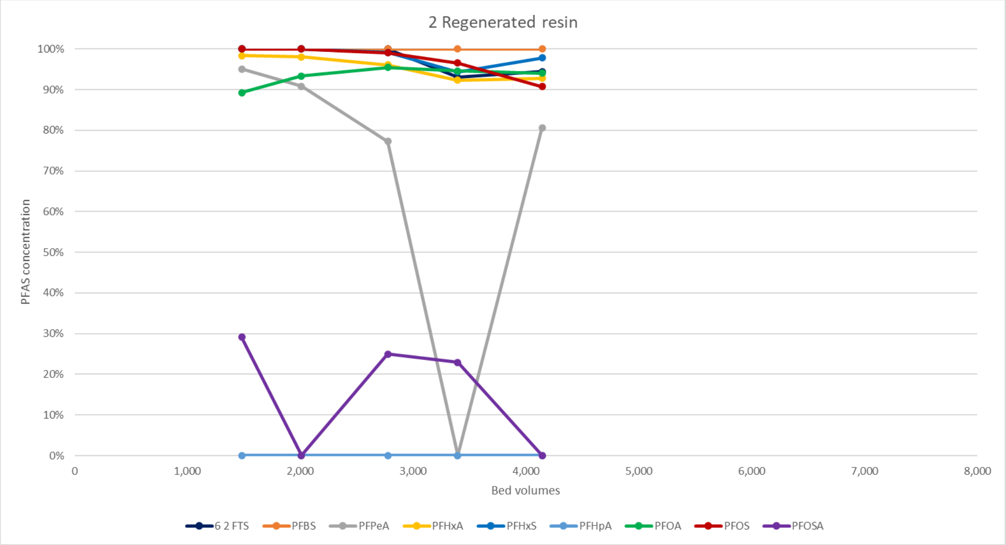


FIGURE 53. PFAS removal percentage as a function of bed volumes in a column containing regenerated resin material.

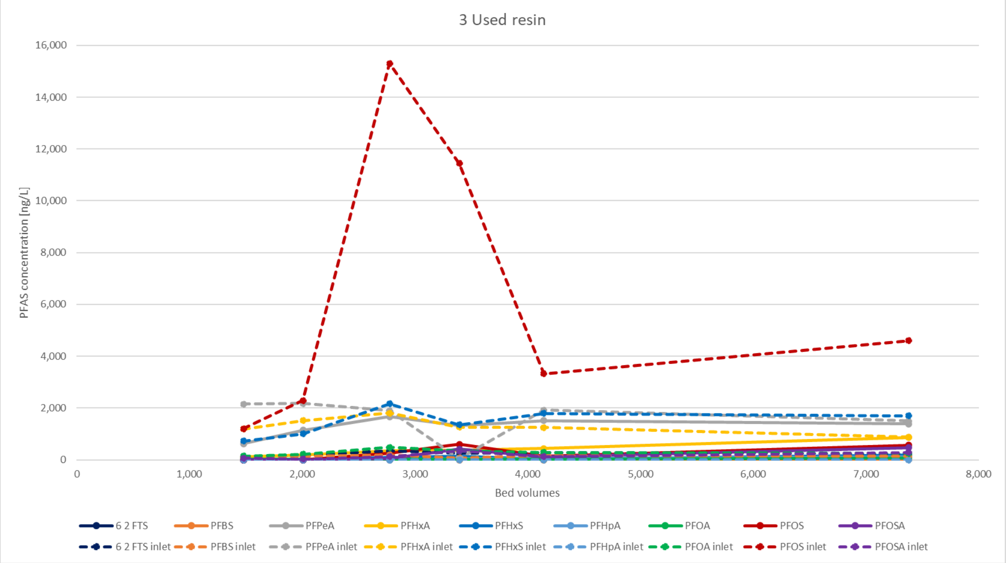


FIGURE 54. PFAS inlet and outlet concentrations of a column containing used resin material. The concentration is plotted as a function of bed volumes through the column.

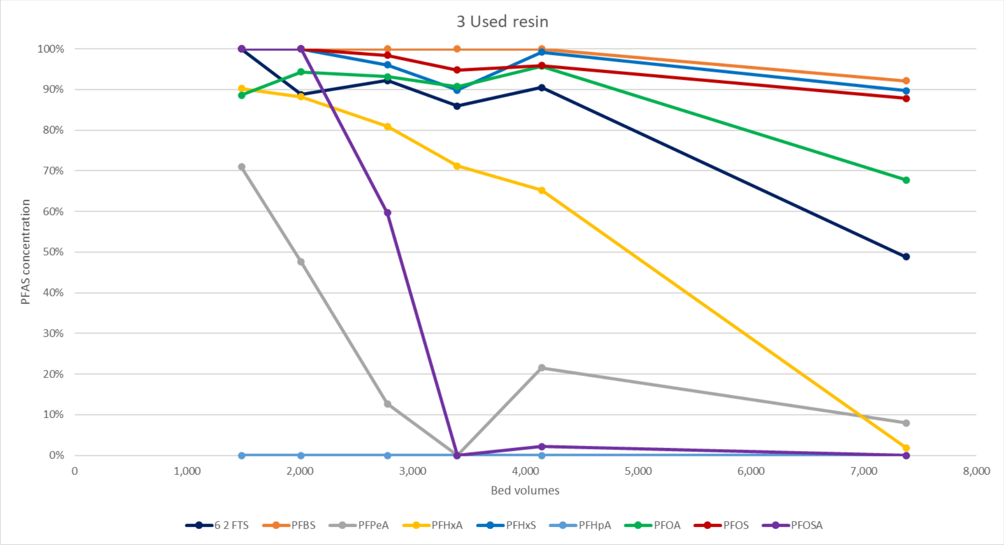


FIGURE 55. PFAS removal percentage as a function of bed volumes in a column containing used resin material.

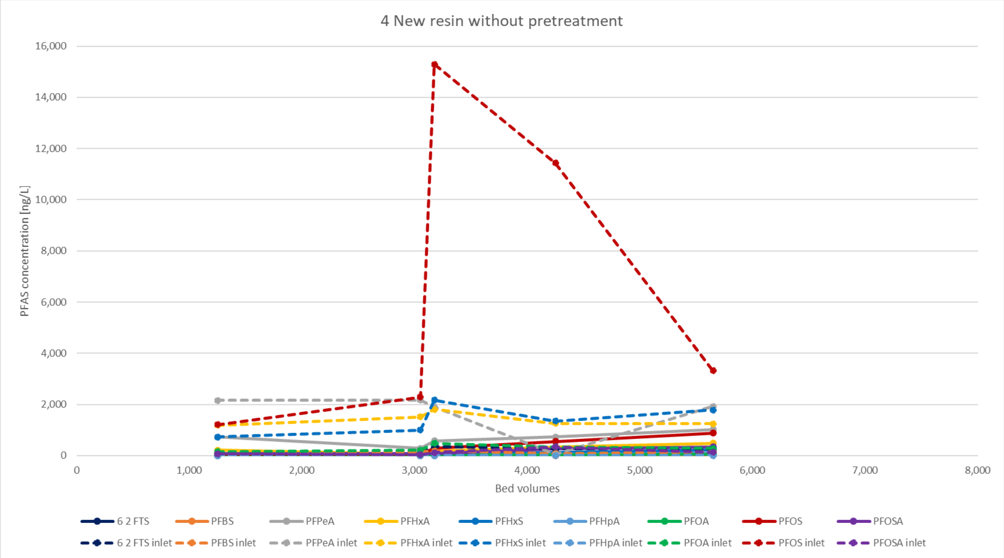


FIGURE 56. PFAS inlet and outlet concentrations of a column containing new resin material, fed with water without pretreatment. The concentration is plotted as a function of bed volumes through the column.

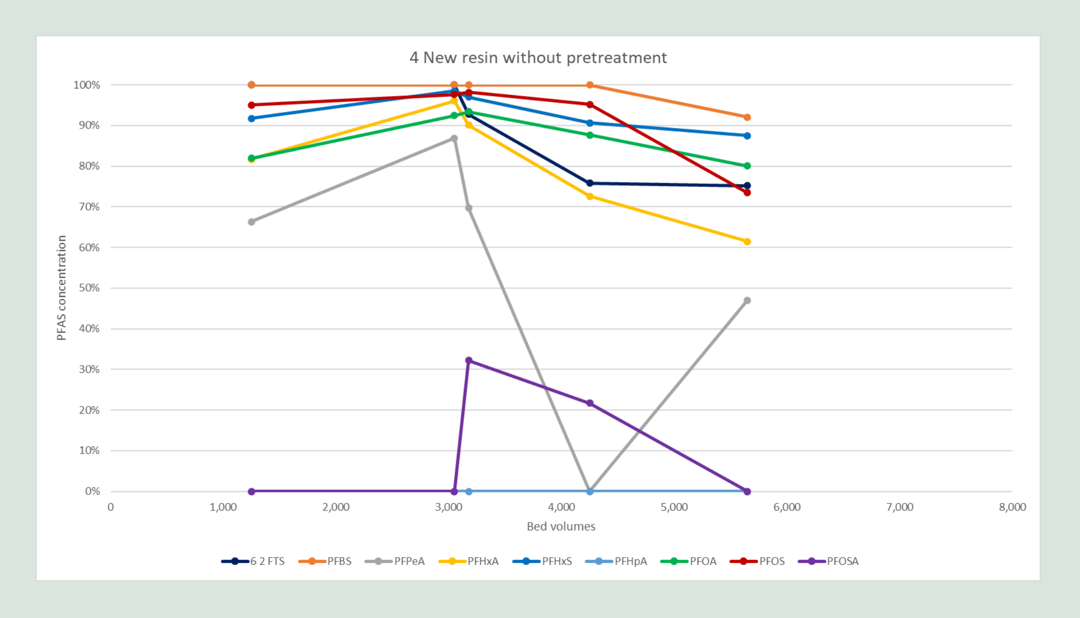


FIGURE 57. PFAS removal percentage as a function of bed volumes in a column containing new resin material, fed with water without pretreatment.

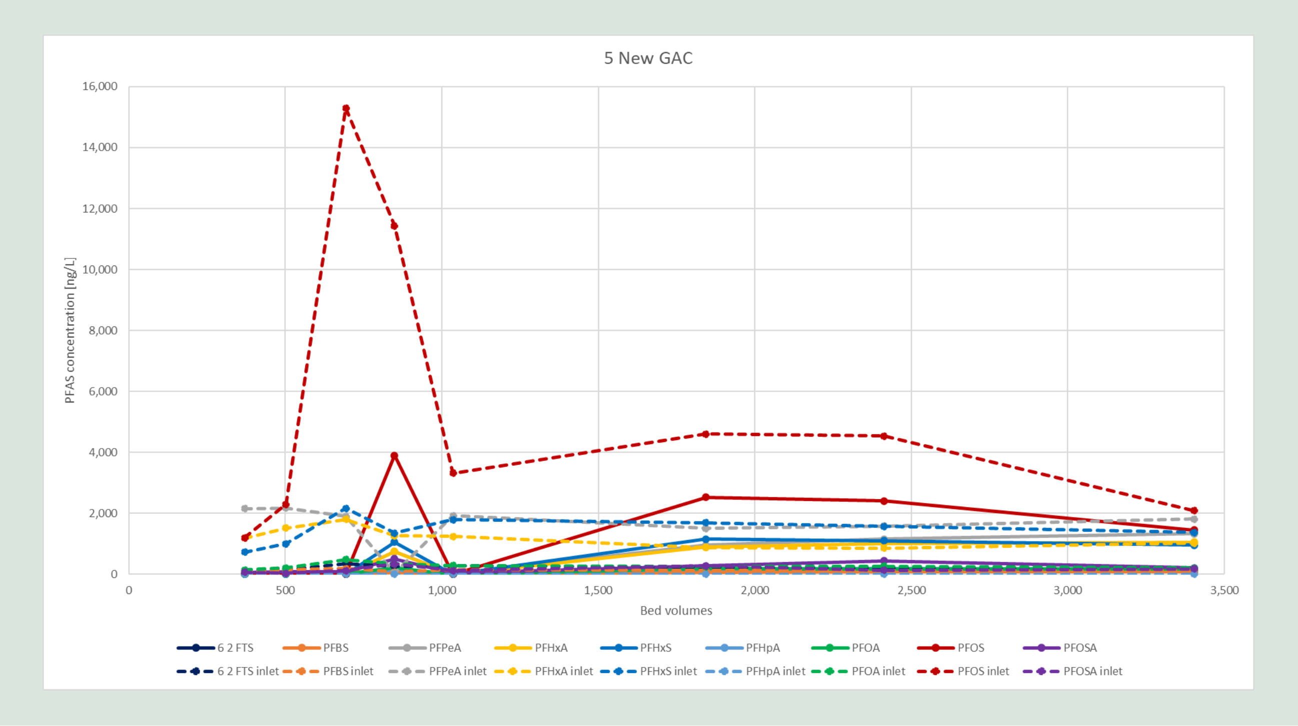


FIGURE 58. PFAS inlet and outlet concentrations of a column containing new GAC material. The concentration is plotted as a function of bed volumes through the column.

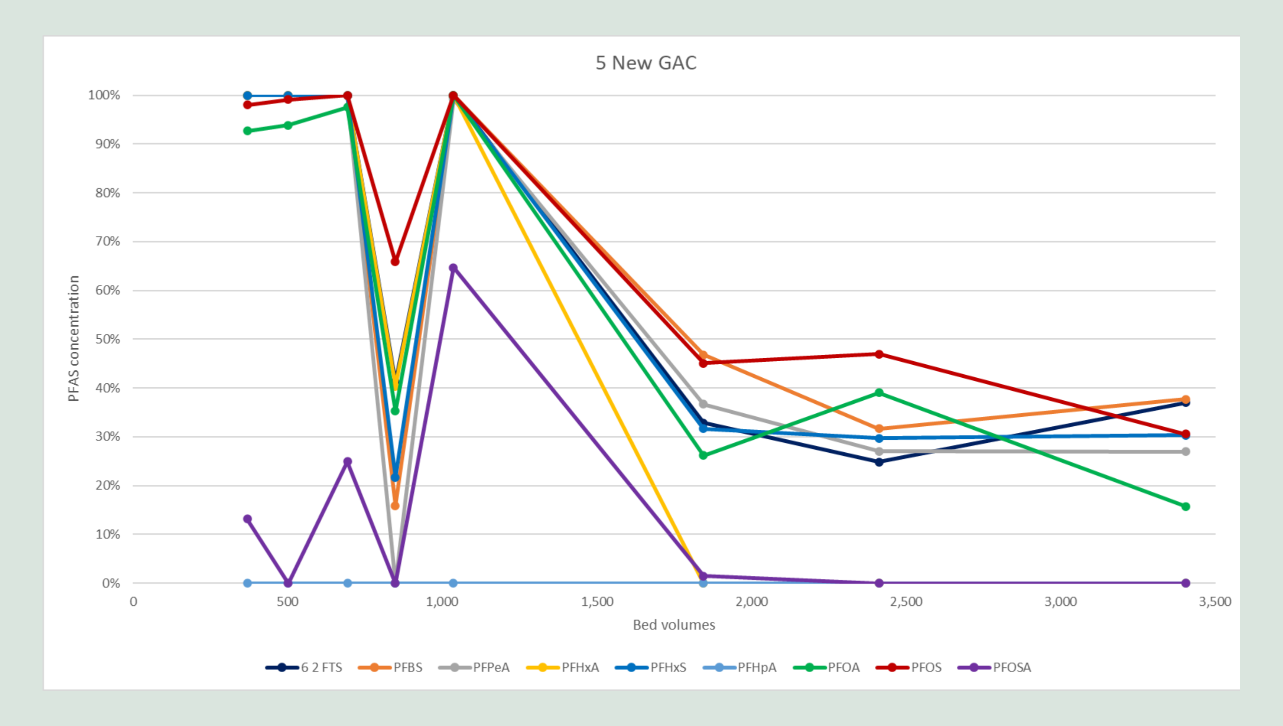


FIGURE 59. PFAS removal percentage as a function of bed volumes in a column containing new GAC material.

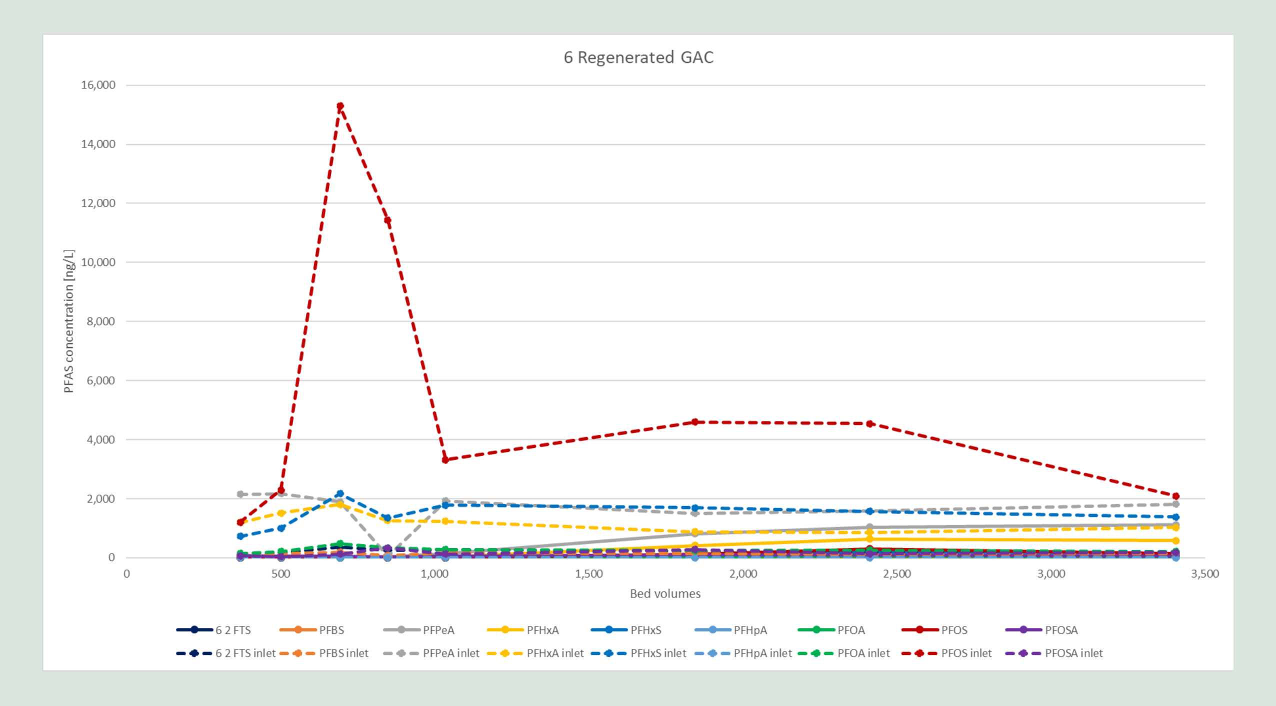


FIGURE 60. PFAS inlet and outlet concentrations of a column containing regenerated GAC material. The concentration is plotted as a function of bed volumes through the column.

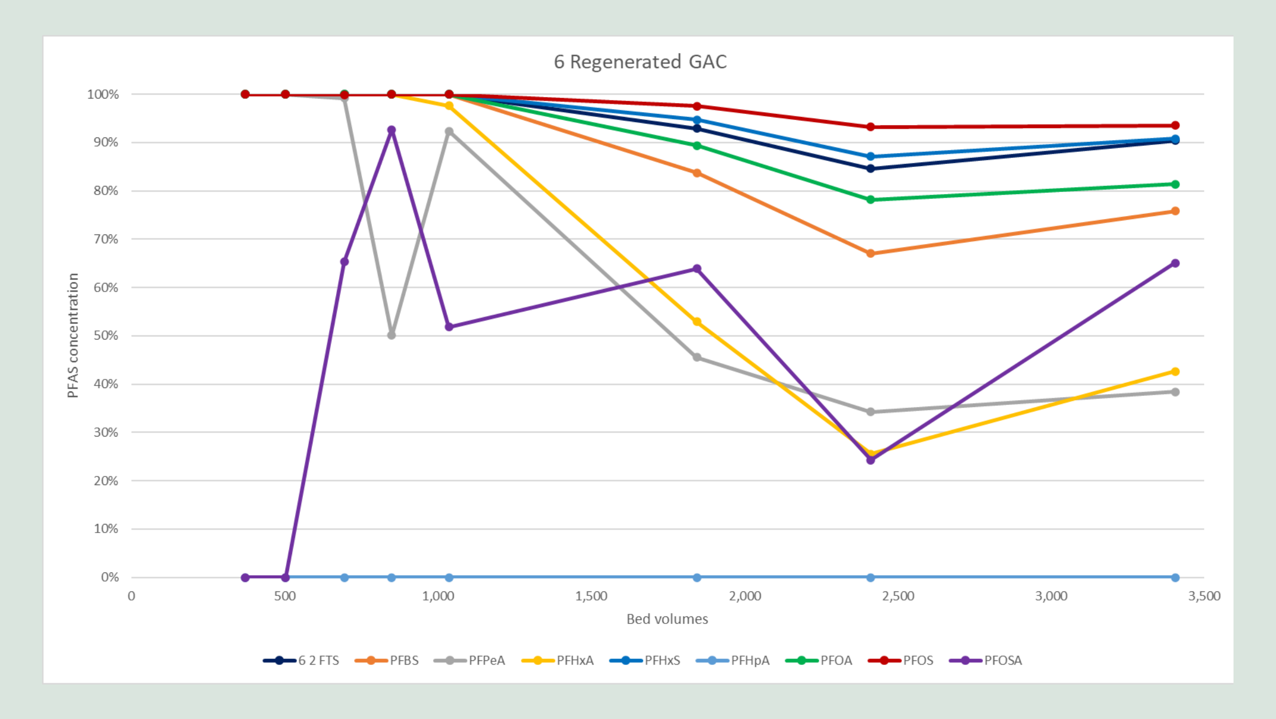


FIGURE 61. PFAS removal percentage as a function of bed volumes in a column containing regenerated GAC material.

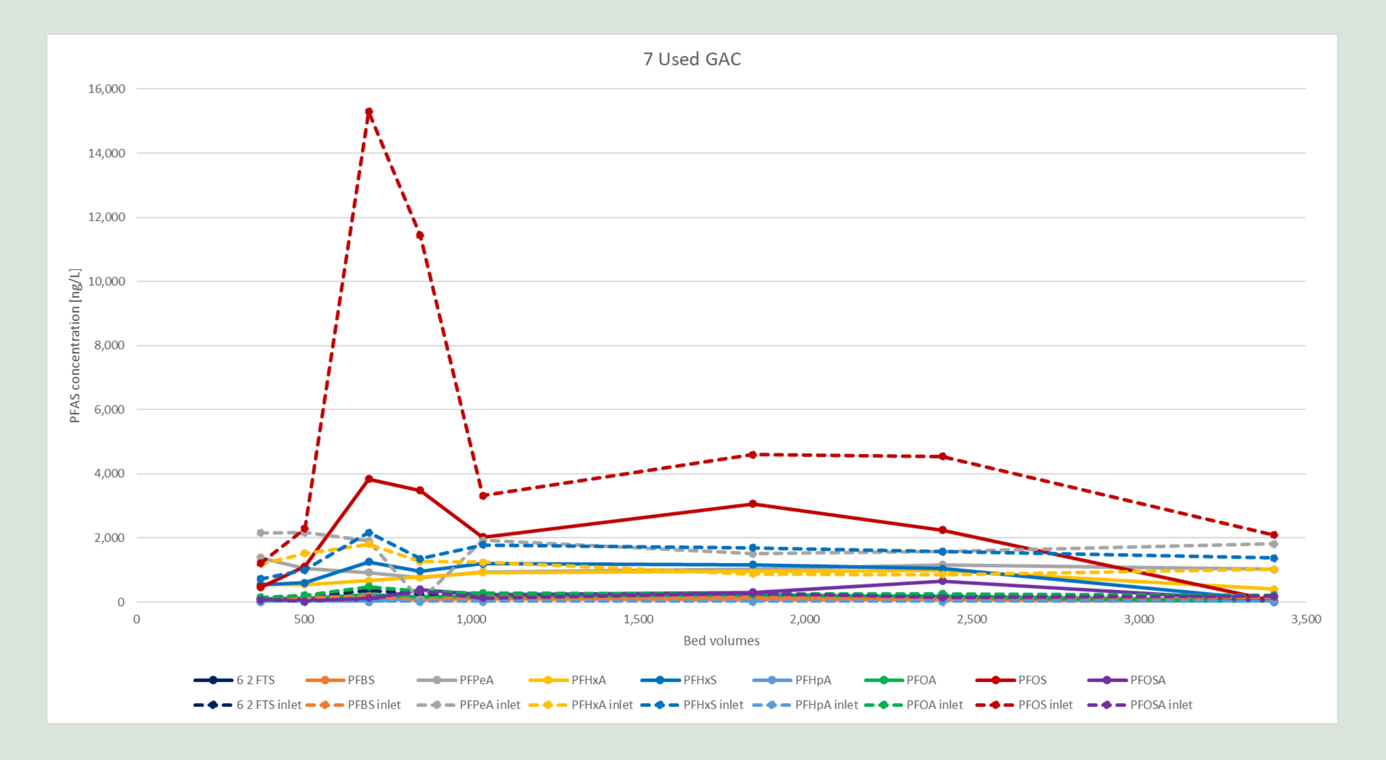


FIGURE 62. PFAS inlet and outlet concentrations of a column containing used GAC material. The concentration is plotted as a function of bed volumes through the column.

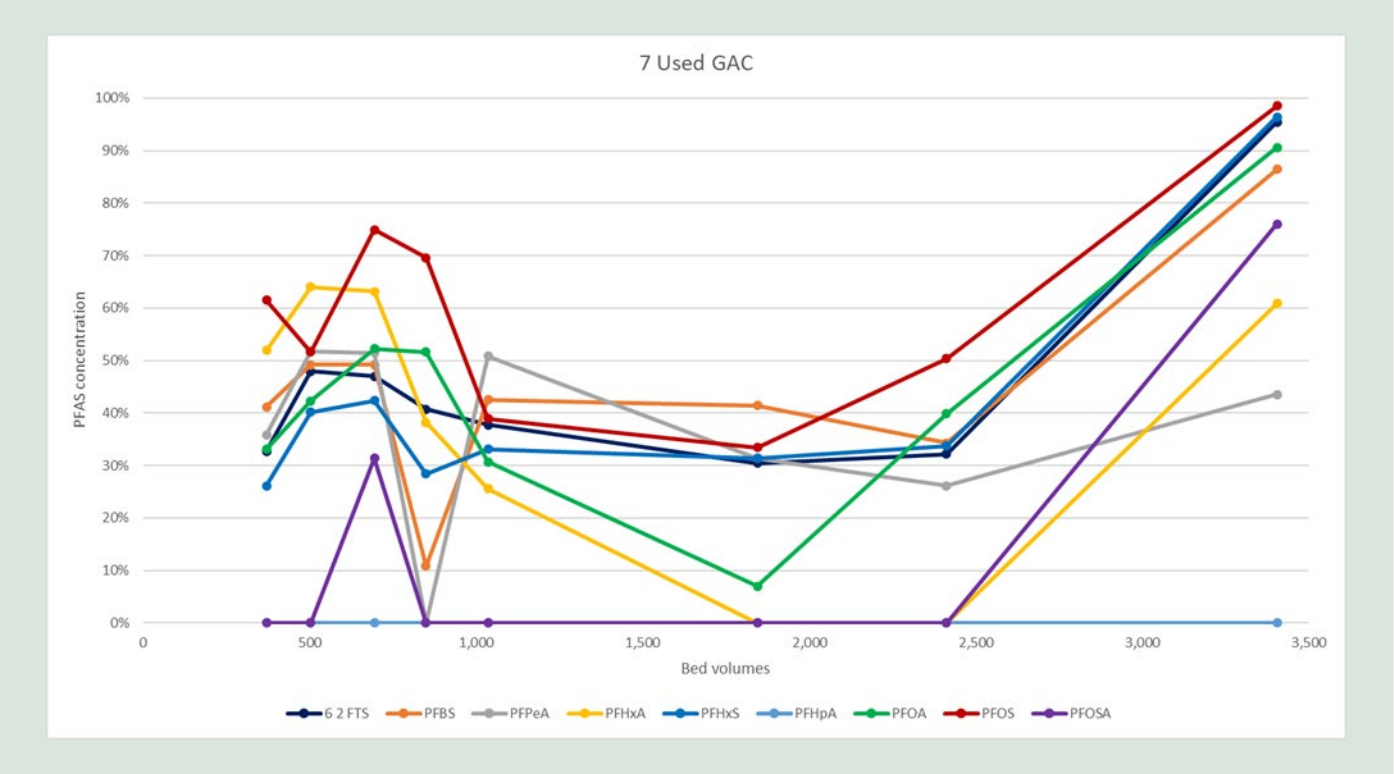


FIGURE 63. PFAS removal percentage as a function of bed volumes in a column containing used GAC material.

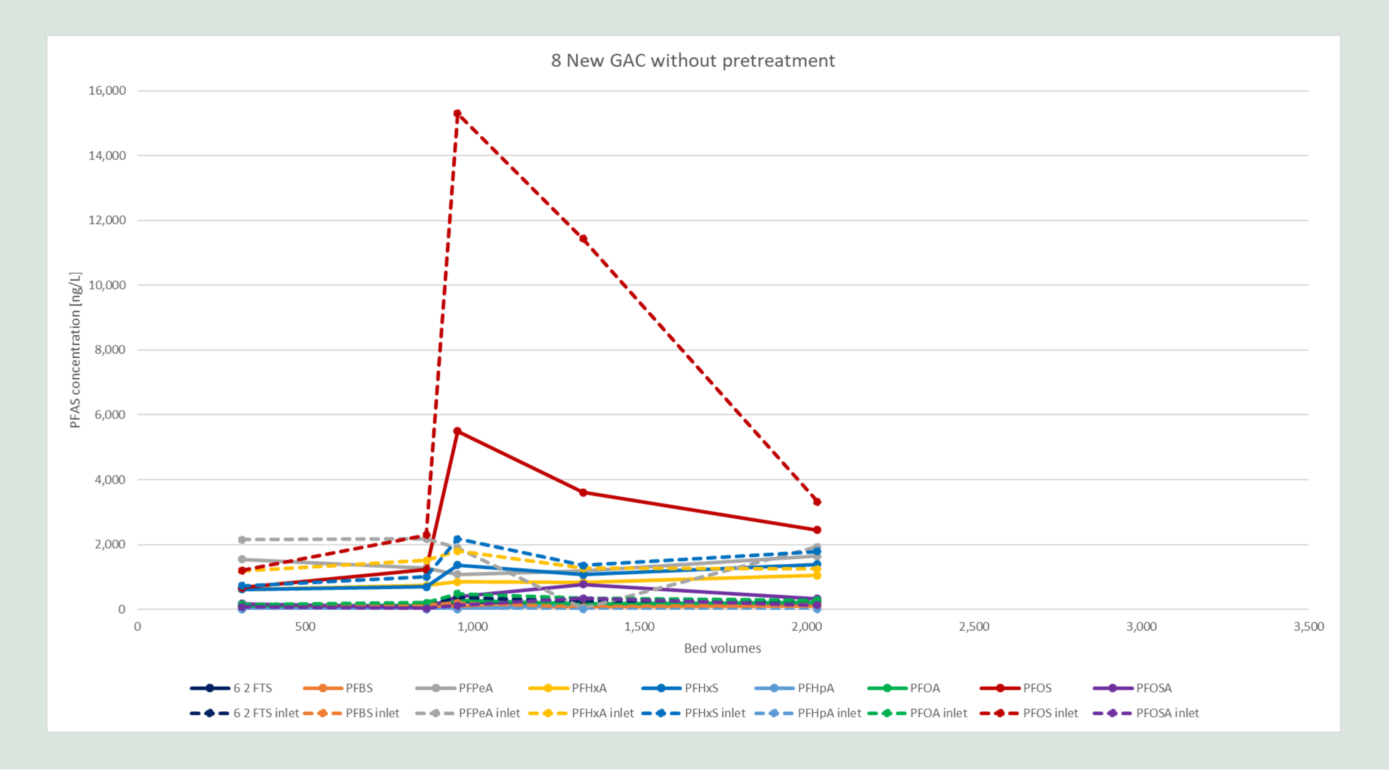


FIGURE 64. PFAS inlet and outlet concentrations of a column containing new GAC material, fed with water without pre-treatment. The concentration is plotted as a function of bed volumes through the column.

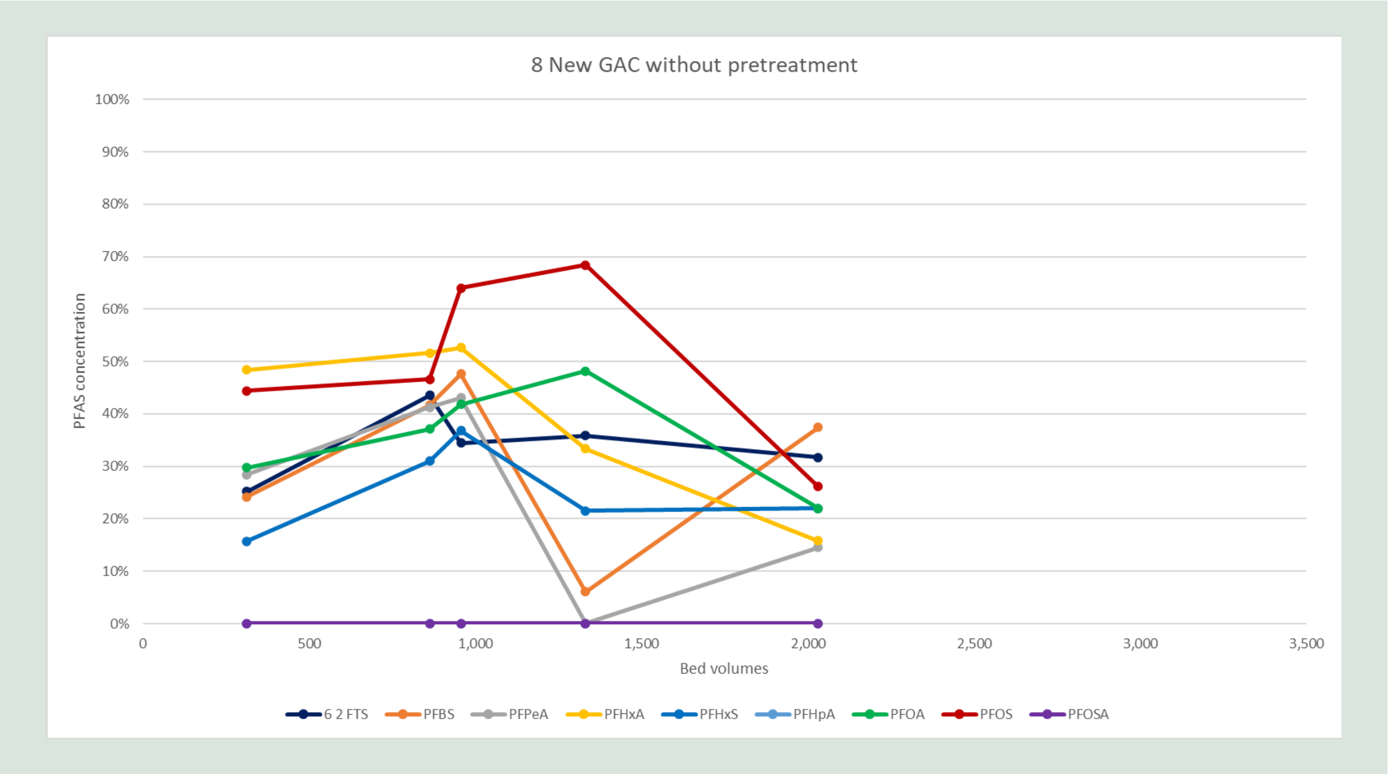


FIGURE 65. PFAS removal percentage as a function of bed volumes in a column containing new GAC material, fed with water without pretreatment.

PFAS-inator

Rapporten giver et overblik over PFAS (Per- and Polyfluoroalkyl Substances) med fokus på deres forekomst, fjernelses- og destruktionsmetoder. Formålet er at forstå variationen af PFAS i perkolat fra lossepladser og de faktorer, der påvirker fjernelseseffektiviteten.

PFAS er menneskeskabte forbindelser kendt for vand- og olieafvisende egenskaber samt høj modstand mod varme og slid, hvilket gør dem svære at destruere. De udgør et stigende miljøproblem fra kilder som industri, lossepladser og brandbekæmpelsesområder. Fjernelse af PFAS er dyrt, og det anbefales at fjerne dem tæt på kilden for at undgå fortynding og øgede behandlingsomkostninger. Hvis kilderne er fortyndet, bør de koncentreres før destruktion.

Behandling af PFAS i losseplads-perkolat sker typisk ved brug af adsorptionsmaterialer som granulært aktivt kul (GAC) og ionbytteresin. Resin har en højere fjernelseseffektivitet end GAC. Kædelængden af PFAS påvirker deres hydrofobicitet, hvor korte kæder er sværere at adsorbere. Organisk materiale i perkolat konkurrerer med PFAS om adsorptionspladser, hvilket kræver forbehandling som koagulation, flotation og membranfiltrering for at forlænge kolonnernes levetid. Fluorescens som parameter til hurtigere gennembrudsanalyse viser potentiale, men kræver yderligere studier.

Kombineret fjernelse af PFAS og tungmetaller har været succesfuld i laboratorieeksperimenter.

Superkritisk vandoxidation (SCWO) er effektiv til PFAS-mineralisering med destruktions-effektivitet over 99,99%, men kapacitet og behandlingshastighed er udfordringer.

Storskala PFAS-behandling er implementeret på flere skandinaviske deponier, hvor behandlingen er overkommelig og kan installeres i containere eller telte.

The Danish Environmental
Protection Agency
Tolderlundsvej 5
DK - 5000 Odense C

www.mst.dk